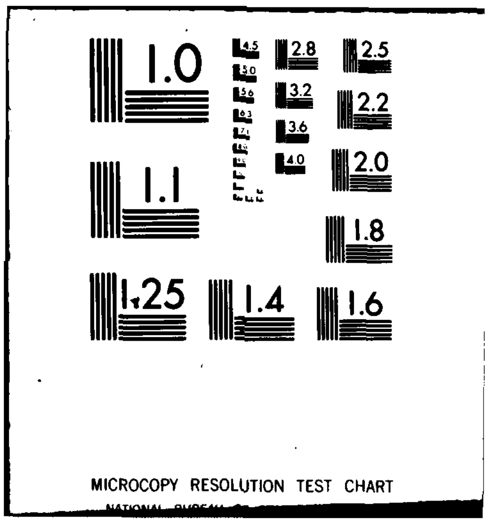
AD-A081 727 AIR FORCE MATERIALS LAB WRIGHT-PATTERSON AFB OH F/G 11/6
FAILURE MECHANISMS AND INTERPHASE CHEMISTRY OF GOLD FILMS ON TI--ETC(U)
JAN 80 W L BAUN
UNCLASSIFIED AFML-TR-79-4178-PT-1 NL

1 of 1

END
DATE
FILMED
4-80
DTIC


1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
MICROCOPY RESOLUTION TEST CHART

14

AFML-TR-79-4178-PT-1
Part I

LEVEL II

ADA081727

6

FAILURE MECHANISMS AND INTERPHASE CHEMISTRY OF GOLD FILMS ON Ti6Al4V
Part I. Surface Chemistry Of Failure Surfaces

10

W. L. BAUN
MECHANICS & SURFACE INTERACTIONS BRANCH
NONMETALLIC MATERIALS DIVISION

11 JANUARY 1980

12 53

16 2417

17 02

9

TECHNICAL REPORT AFML-TR-79-4178, Part I
Final Report for period July 1978 to October 1979

AIR FORCE MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

012320

NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever, and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not be be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporations, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

This report has been reviewed by the Information Office (OI) and is releasable to the National Technical Information Service (NITS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

W. L. BAUN, Project Engineer
Mechanics & Surface Interactions Br.
Nonmetallic Materials Division

S. W. TSAI, Chief
Mechanics & Surface Interactions Br.
Nonmetallic Materials Division

FOR THE COMMANDER

J. M. KELBLE, Chief
Nonmetallic Materials Division

"If your address has changed, if you wish to be removed from our mailing list, or if the addressee is no longer employed by your organization, please notify AFML/MBM, W-PAFB, Ohio 45433 to help us maintain a current mailing list".

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

AIR FORCE/56780/20 February 1980 — 200

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFML-TR-79-4178, Part I	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Failure Mechanisms and Interphase Chemistry of Gold Films on Ti6Al4V		5. TYPE OF REPORT & PERIOD COVERED Internal July 1978 to October 1979 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) W. L. Baun		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Air Force Materials Laboratory Air Force Systems Command Wright Patterson Air Force Base, Ohio 45433		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Project 2419, Task 241902, WU # 44
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Materials Laboratory (AFML/MBM) Air Force Wright Aeronautical Laboratories Wright Patterson Air Force Base, Ohio 45433		12. REPORT DATE January 1980 13. NUMBER OF PAGES 53
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified 15a. DECLASSIFICATION DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for Public Release Distribution Unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Adhesive Bonding, Ti6Al4V, Surface Treatments, Surface Chemistry, Gold, Vapor Deposited, Failure Mechanisms, Weak Boundary Layer, Locus of Failure		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This work is part of a program which looks at the effects of surface treatments on surface chemistry and morphology of titanium alloys with reference to adhesive bonding. Here gold is vapor deposited on Ti6Al4V which was prepared to simulate conditions of etching and aging which might be encountered during processing and use. Although this model system of gold on Ti6Al4V is not a direct analogy to adhesive bonding, certain similarities do exist and the (cont'd)		

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

20. (cont'd)

system provides interesting information on bond failure mechanisms. Surface chemical analysis using ISS/SIMS showed that the gold on titanium alloy could model the failure mechanisms on surfaces prepared by methods similar to that in adhesive bonding. ISS/SIMS was found to be a sensitive chemical method to determine locus of failure and the change of composition at interfaces following humid aging and bond testing. Several types of failures appeared to be observed. Fractures which appeared to have occurred by interfacial failure were actually found to be mixed mode failures or failures in a weak boundary layer. It was found that the chemistry of different etches as well as the vacuum evaporation conditions affected the adhesion of gold to titanium 6 aluminum 4 vanadium. Slow evaporation of the gold in ultra high vacuum onto a heated (180°C) substrate formed the most durable and best adhering gold films.

FOREWORD

This technical report was prepared by W. L. Baun of the Mechanics and Surface Interactions Branch, Nonmetallic Materials Division, Air Force Materials Laboratory (AFML/MBM), Wright Patterson Air Force Base, Ohio. This work was initiated under Project 2419 "Non-Metallic and Composite Materials" and work unit directive number 44 "Improved Materials Processes and Life Prediction Methodology for Adhesive Bonding". The work unit monitor was Dr. T. W. Haas.

Valuable discussion with N. T. McDevitt is acknowledged. Gary Fugate and Donald Thomas are thanked for careful experimental work. Some bonding and testing of specimens was capably carried out by A. K. Behme, Jr. The AES elemental profile was prepared by J. S. Solomon.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS (Cont'd)

SECTION I

INTRODUCTION

Much of the emphasis thus far in the preparation of metal surfaces for adhesive bonding has been for aluminum and aluminum alloys because they are currently in use in commercial and military aircraft. However, as applications constantly increase for stronger, lighter materials operating at higher temperatures, a need for surface preparations for adhesive bonding of titanium and titanium alloys has evolved. Surface treatments such as etches[(1)], abrasive slurries[(2)], and anodization[(3)] techniques to form thin and thick films have been developed. Previously in the work in this laboratory various chemical treatments have been evaluated[(4,5,6)]. In the segment of work presently being reported here, a model system is used to evaluate Ti6Al4V failure mechanisms and interphase chemistry. It is hoped that this model system in which thin, uniform gold films are evaporated on the alloy surface will provide fundamental interphase data and remove some of the variabilities caused by the adhesive itself. Commercial adhesives are complex proprietary mixtures which are difficult to characterize. They are also difficult to detect in small amounts on the surface. It is recognized that the adhesion of gold to titanium is not a direct analogy to adhesive bonding, but certain similarities do exist. In addition, the adhesion of thin metal films to other metals and oxides is of importance in other technologies such as the semiconductor industry.

SECTION II
EXPERIMENTAL

The gold was evaporated from a tantalum boat in an ultra-high vacuum commercial evaporator at pressures of less than 10^{-7} Torr. The exact conditions for rate of evaporation (substrate temperature, etc.) is given with the sample in the text if it is considered pertinent. Thicknesses of the gold were estimated using a quartz crystal oscillator.

A series of experiments were performed in which deposition conditions were altered to determine the effect on gold adhesion. These experiments will be reported separately but may be summarized as follows: best adhesion of the gold was obtained at the best vacuum possible, on heated substrates (180°C). The deposition rate had little effect on adhesion characteristics.

The surface chemistry of the alloy surfaces was characterized both before and after testing by ion scattering spectrometry (ISS) and secondary ion mass spectrometry (SIMS). This dual method uses a low energy ion beam (1-3 kev) to probe the surface. The ISS method (3M Company, St. Paul, Minnesota) measures the energy loss when the probing ion scatters from the outermost layer at the surface. The SIMS technique measures the mass spectrum of the sputtered ions which are removed from the surface by the primary ion beam. Advantages and operating parameters were outlined in an earlier report [7] and the experimental set-up was shown in our earlier reports and papers[4,5,6,7]. Surface morphology of some specimens was studied using a scanning electron microscope, but will not be discussed here.

TABLE I

ADHESION OF GOLD ON Ti6Al4V ALLOYS TREATED IN DIFFERENT WAYS

Sample No.	Treatment	Purpose	Result of Tape Test
230-1	Boiled 30 min in Tap H_2O	Form WBL	All Au Removed
230-2	Heated 30 min @ 500^oF (air)	Form Alkali WBL	All Au Removed
230-3	Etched 2 min $HF/H_2NH_4PO_4$ (25ml/50gl/975m/H_2O	Etch Surface	Very slight Au Removal
230-4	Etched 2 min $H_2Si_4F_6$*	Etch Surface	All Au Removed
230-5	Etched 2 min HF Si, Anod. 50V phth**	Etch & Anod.	All Au Removed
230-6	Cleaned SB+D***, 2 hrs UV	Clean Surface	All Au Removed
230-7	As Received	Original Surface	All Au Removed
230-8	As Received, tape pulled from surface	Add organic contam	All Au Removed
230-9	Anodized 20V in $H_2Si_4F_6$	Form WBL at oxide/alloy inter-face	No Au Removed

*Hydrofluosilicic acid 15%, H_2O Sol'n

**Phthalic acid, 2g./l, H_2O Sol'n

***Abrasive Pad & Detergent with Tap H_2O

SECTION III

RESULTS AND DISCUSSION

In order to determine the capabilities of ISS and SIMS to deduce the locus of failure on these specimens, the samples were given various treatments shown in Table I to produce different types of failures. For instance, in 230-1 and 230-2 an attempt was made to form weak boundary layers of impurities at the interface between the gold and the titanium. Previous experience had shown that long exposure of titanium to hot tap water results in the formation of a layer which contains the elements commonly found in the water. Similarly, in 230-2, heating of the specimen at about 500°F in air results in grain boundary diffusion of alkali elements, such as sodium and potassium to the surface with subsequent oxidation. Following the surface treatments and evaporation of the gold on the surface, a tape test was performed as shown in Table I. After the tape test, the specimen was placed in a chamber in which condensing steam media surrounded the gold film. Specimen temperature was approximately 90°C. Specimens were held under these conditions for 48 hours. A second tape test similar to the first was then carried out. Results of this tape test are shown in Table II. Surfaces following each of these steps were then evaluated by ISS and SIMS. Results of ISS and SIMS data are shown for sample 230-1 in Figure 1. This specimen which was boiled in tap water for 30 minutes shows the accumulation on the surface of the elements present in the water. The ion scattering spectrum shows oxygen and the unresolved spectra from many of the elements, such as magnesium, aluminum, silicon, potassium, calcium, and titanium. A small iron impurity is also observed. The positive SIMS spectrum shows the real utility of this technique as a complement to ion scattering in that the mass unit resolution now allows the

TABLE II

EFFECT OF CONDENSING STEAM ON
ADHESION OF GOLD ON Ti6Al4V SAMPLES
SHOWN IN TABLE I

Sample No.	Results of Tape Test 2	Adhesion Change From Test 1
230-1	Mostly All Au Removed	Slight increase
230-2	All Au Removed	No change
230-3	No Au Removed	Increase
230-4	Some Au Removed in Spots	Increase
230-5	Nearly All Au Removed	Slight increase
230-6	All Au Removed (very easy)	No change
230-7	Nearly All Au Removed	Slight increase
230-8	Some Au Removed	Increase
230-9	No Au Removed	No change

separation of near atomic number elements, such as sodium, magnesium, aluminum, silicon, and the group potassium, calcium, and titanium. The same surface, following the initial tape test, is shown in Figure 10. The figures are arranged to show the sequence of the original surfaces followed by the titanium after the Au strip and then the Au surface is shown following this strip. Finally, the titanium from the stripped surface following the exposure to steam is shown and then the matching gold surfaces after this steam exposure are shown. In some cases interfacial failure did not occur and so spectra could not be shown for these failure surfaces. An example, then, of a series showing the same surfaces and interfaces following the tape test is shown in Figures 1, 10, 16, 22, and 28. Note in the specimens following testing compared to the original specimens that basically in the weak boundary layer the same element exists but the ratios of these elements vary from sample to sample. Note also in the samples in which the SIMS spectrum is obtained from gold on the tape that lithium is always observed. Lithium is a highly mobile ion placed on the tape in the form of a proprietary compound to keep the tape from sticking to itself. As can be seen from the figures in the specimens in which a weak boundary layer was purposely created failure does take place in this weak boundary layer. Note also that on the failure surfaces some amount of gold remains and the gold is easily identified by the ion scattering spectrum. The presence of gold on the weak boundary layer suggests a mixed mode failure has occurred. This is similar to many adhesive bond failures where the failure occurs along an irregular area which contains elements of both the adherend and adhesive. The SIMS spectrum also shows the redistribution of elements. Spectra from the gold surfaces stripped from the sample during the tape test also suggest that significant amounts of the elements in the weak boundary layer remain on the gold. In addition to the appearance of these elements in the spectrum it is evident that significant coverage exists on

the surface due to the observation of attenuation of the gold signal. An example of this attenuation is shown in Figure 16. Here first the ion scattering spectrum is shown with the rate meter set at 100,000 counts per second full scale which would normally be obtained from the gold if it were not contaminated. It can be seen that the spectrum that was obtained from this surface is approximately 10 times smaller. The Au atoms apparently are shielded by the elements in the weak boundary layer which are now on the gold surface.

The specimen heated in air at 500^{o}F shows large amounts of sodium and potassium on the surface along with the alloy elements aluminum and vanadium as shown in Figure 2. The ISS spectrum observed following the tape test is shown in Figure 11. It shows only a small trace of gold present on the surface and apparent failure within this weak boundary layer containing alkali elements. In many adhesive bonded specimens showing apparent interfacial failure this same alkaline rich weak boundary layer is often present. Perhaps in some cases these alkali elements diffuse to the surface by grain boundary migration during curing of the adhesive bond. The gold surface shown in Figure 17 also contains large amounts of alkali metals although the ratio of sodium and potassium is changed. The meaning of this change is not known.

Numerous interesting features were observed in the spectra from the samples treated in different ways. For instance, in Figure 3 from the specimen etched in $HF/H_2NH_4PO_4$ the phosphorous, normally not particularly sensitive in positive SIMS, is observed along with the cluster ion PO^+. In addition, the ion scattering spectrum does not show the characteristic pattern of titanium oxide. The surface after the gold was removed is shown in Figure 12 and indicates virtually complete gold coverage. The SIMS spectrum shows fluorine, aluminum, and titanium on the gold surface suggesting either the removal of gold in slight patches or the diffusion of those elements

through the gold. The treatment given to sample 230-5 which included anodization in phthalic acid at 50 volts shows in the SIMS spectrum a large intensity of TiO+ compared to Ti+. Such intensities of the molecular species observed in the SIMS spectrum may be an important clue to the activity and bondability of titanium surfaces. Other changes in the molecular cluster spectra such as the increased amount of TiOH+ or the apparent change in molecular species from oxides to fluorides may be equally important. Such a suggestion is shown in Figure 9 where CaF+ ions at mass 59 and TiF+ ions at mass 67 are observed from the spectra obtained from the surface of the sample anodized in hydrofluosilicic acid. The presence of fluorine on the surface and at the failure interface is to be avoided. It was found in previous work that an anodized oxide could be prepared in a fluorine containing bath to produce a film having fluorine concentrated at the interface and consequently a weak boundary layer. If these surfaces are bonded with a strong adhesive such as an epoxy and caused to fail, particularly in a test showing pure sheer, the failure usually takes place along this weak boundary layer between the metal and the oxide. Following both tape tests gold was removed from the oxide surface and failure did not take place at the oxide metal interface. Apparently the peel test does not place sufficient stress on the interface. Paradoxically, however, the gold adheres much better to this anodized surface than to the surfaces prepared chemically. When these gold coated anodized surfaces were bonded with a stronger adhesive and the specimens flexed to produce sheer at the interface then failure did take place at the oxide metal interface. These results point out the necessity of having the proper test to determine effects of surface preparation on bonding.

The fluorine on failure surfaces of the aforementioned specimen is obvious in the ISS spectra of Figure 33. These surfaces were sputtered with several inert gases and elemental

profiles prepared by Auger Electron Spectrometry. These elemental profiles show in addition to the concentration of fluorine at the oxide metal interface that the adhesive has penetrated into the oxide at appreciable distance beyond the original interface. Such an AES elemental profile is shown in Figure 34. This is a compound AES profile produced by sputtering the metal failure surface and the oxide failure surface.

Each of the treatments shown in the accompanying data resulted in specimens which failed at the interfaces which were expected although the easy interfacial failure of surfaces exposed to UV/O_3 is not understood. Only surfaces etched with $HF/H_2NH_4PO_4$ along with the anodized surface mentioned earlier showed any reasonable adhesion. Exposure to condensing steam with the sample near 100^oC results in improvement in the adhesion except where alkali rich boundary layers exist or where adhesion was good and no gold was removed initially.

This improvement of peel strength with exposure to high temperature and humidity has the opposite affect normally obtained with adhesive bond on treated titanium specimens. Longer exposures to high temperatures and humidity did show degradation of bonding in other specimens. Exposure to high temperatures (dry) showed enhancement of bond strength probably due to diffusion mechanisms. Perhaps in this series we are observing an initial improvement which would be followed by degradation. It may also be that the simple peel test is not definitive for the surface treatments used here.

SECTION IV

CONCLUSIONS

This initial set of specimens in which adhesive bonding was modeled by gold adhesion showed that surfaces could be prepared which produced failures similar to those found in adhesive bonding. ISS/SIMS was found to be a sensitive method to determine locus of failure and the change of composition at interfaces following bond testing. Failures which appeared to be adhesive actually were found to be mixed mode failures or failures in a weak boundary layer. Experiments in modeling adhesive bonding will be continued using different treatments and gold evaporation conditions.

REFERENCES

1. T. Smith and D. H. Kaelble, AFML-TR 74-73, June 1974.
2. G. W. Lively, AFML-TR-73-270 Part I, January 1974 and Part II, August 1975.
3. Y. Moji and J. A. Marceau, U.S. Patent 3,959,091, May 25, 1976.
4. W. L. Baun, AFML-TR-76-29, Part I, March 1976.
5. W. L. Baun and N. T. McDevitt, AFML-76-29, Part II, May 1976.
6. W. L. Baun, N. T. McDevitt and J. S. Solomon, AFML-TR-76-29, Part III, September 1976.
7. W. L. Baun, AFML-TR-76-30, March 1976.
8. W. L. Baun, "Formation of Strippable Films on Ti, Ta, and W", AFML TR 79- (to be published).

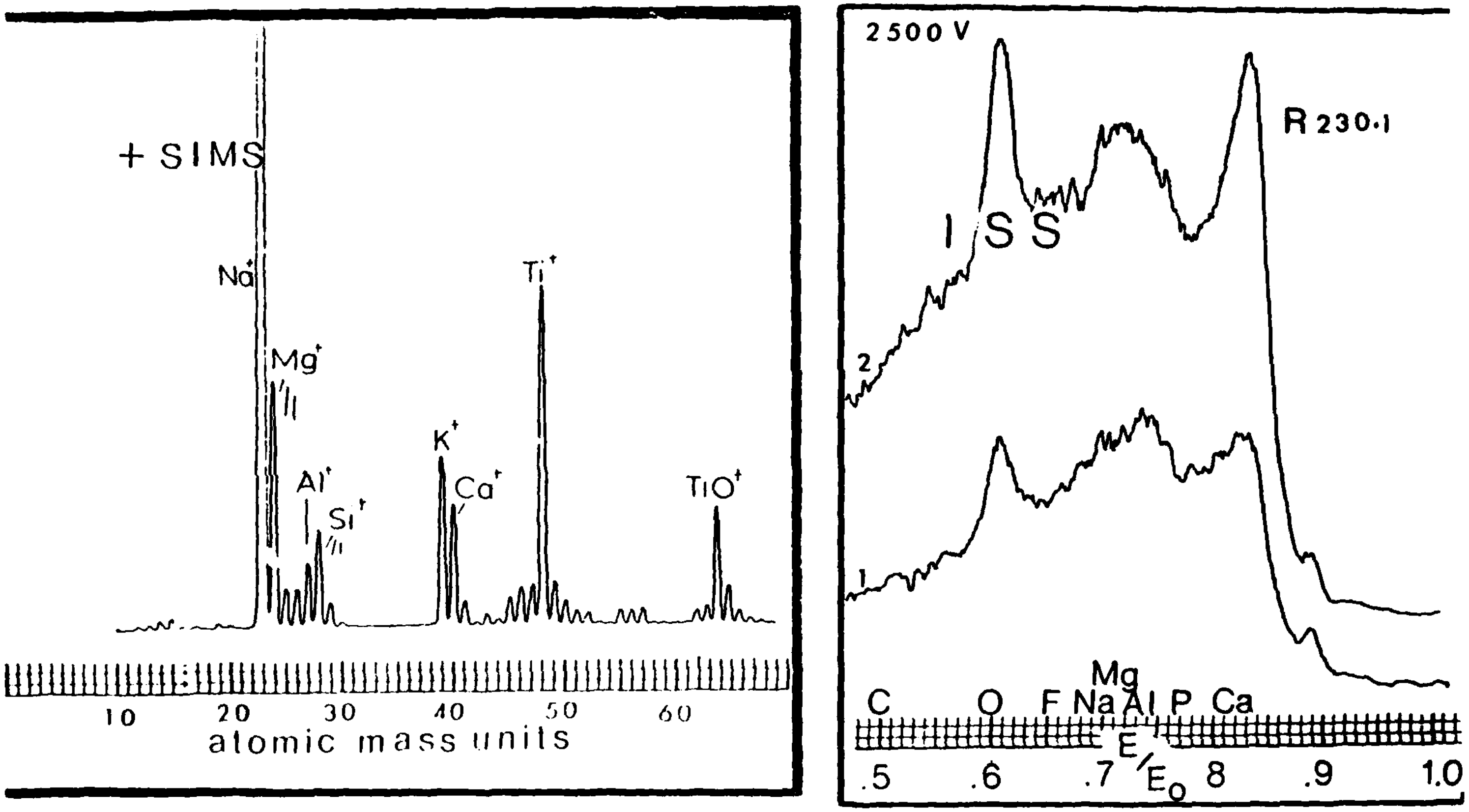


Figure 1. ISS/SIMS Data from Sample 230-1

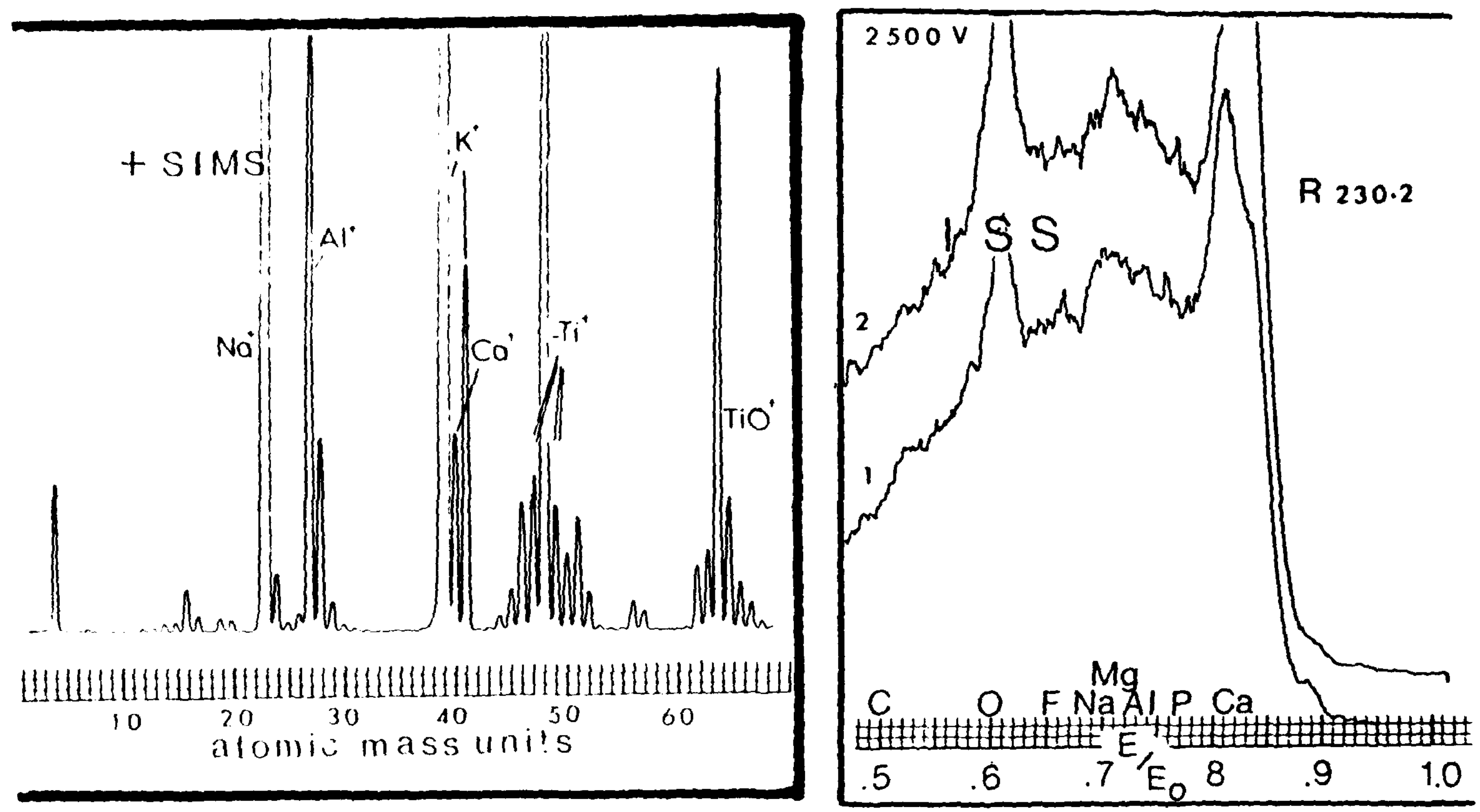


Figure 2. ISS/SIMS Data from Sample 230-2

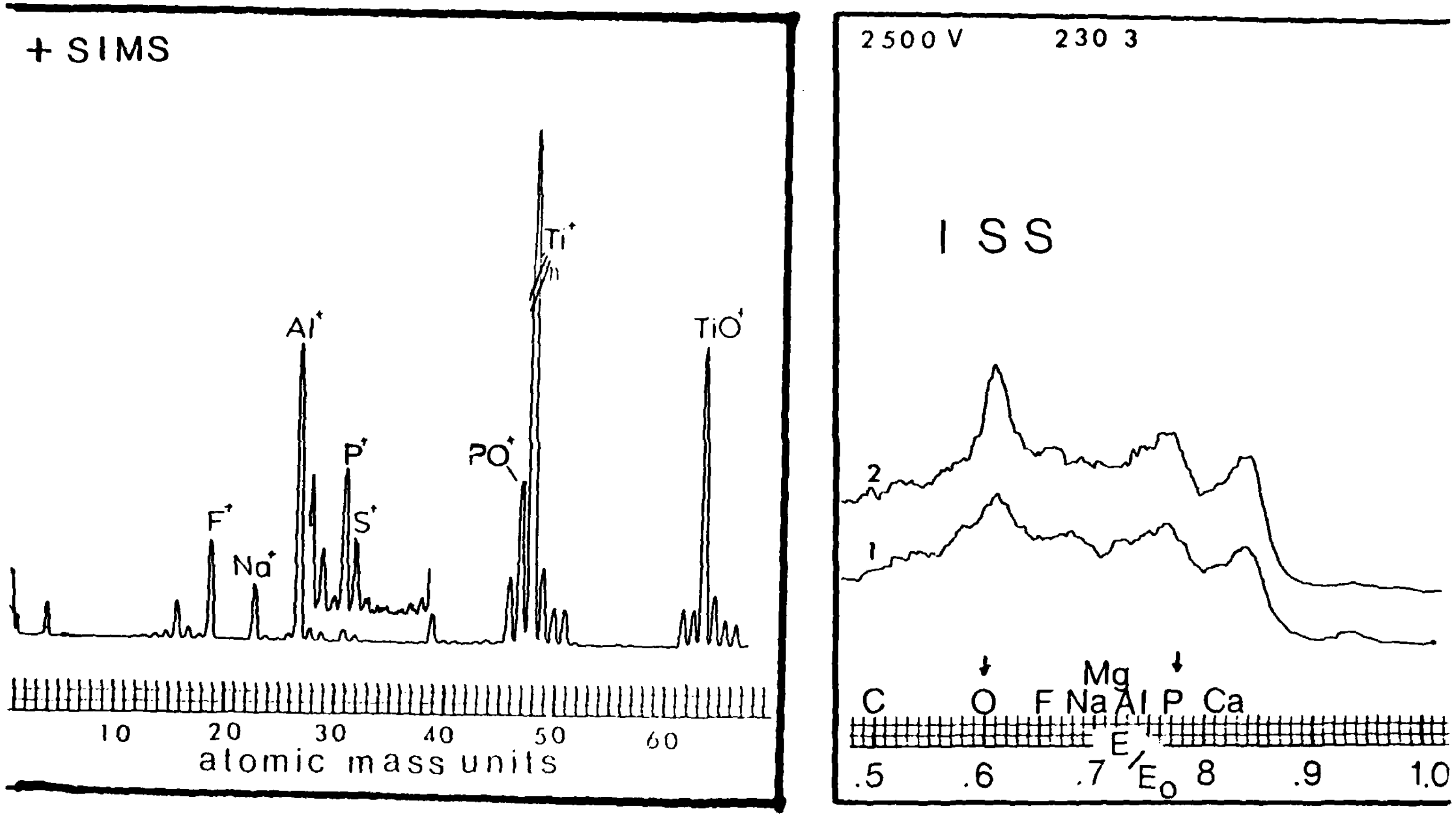


Figure 3. ISS/SIMS Data from Sample 230-3

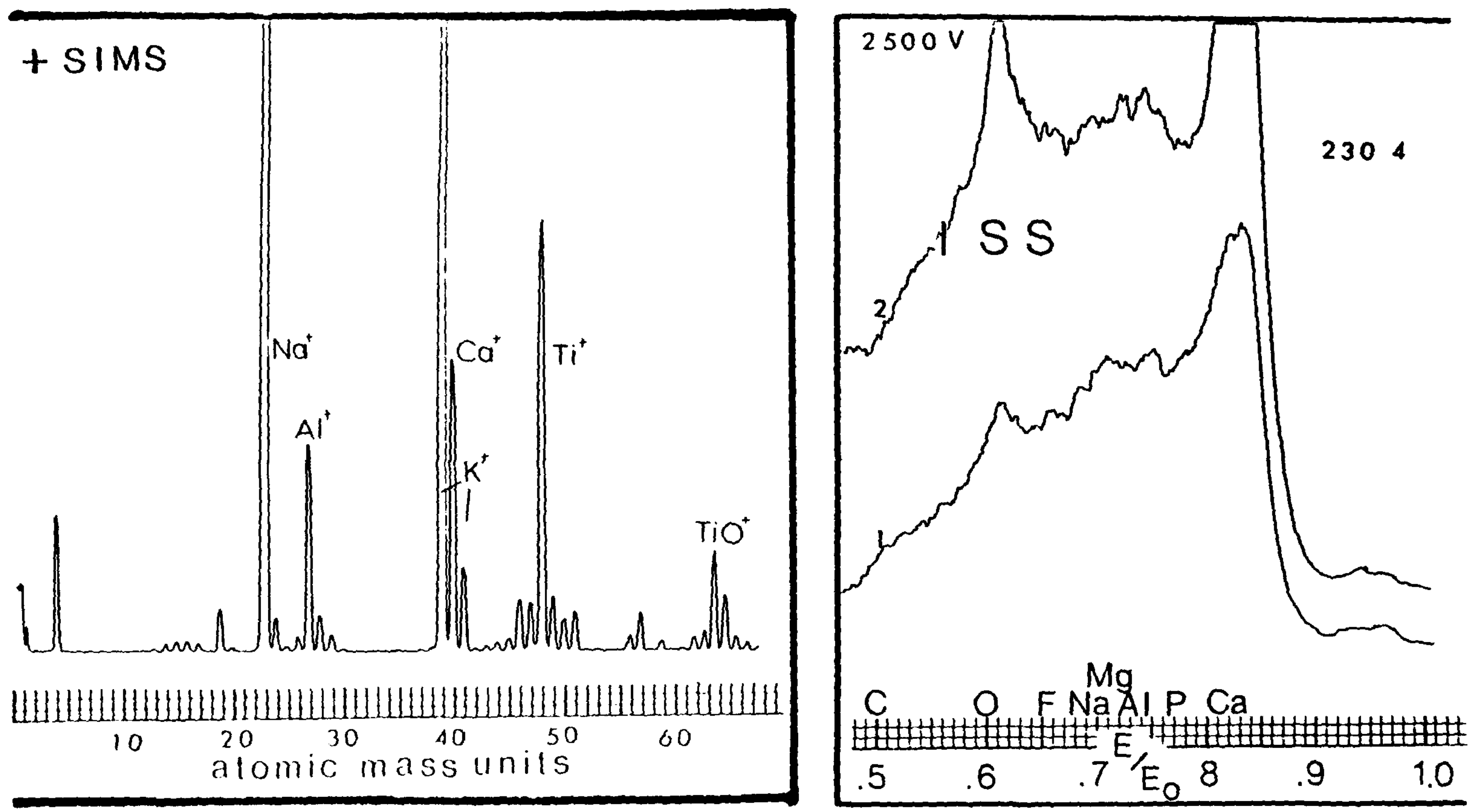


Figure 4. ISS/SIMS Data from Sample 230-4

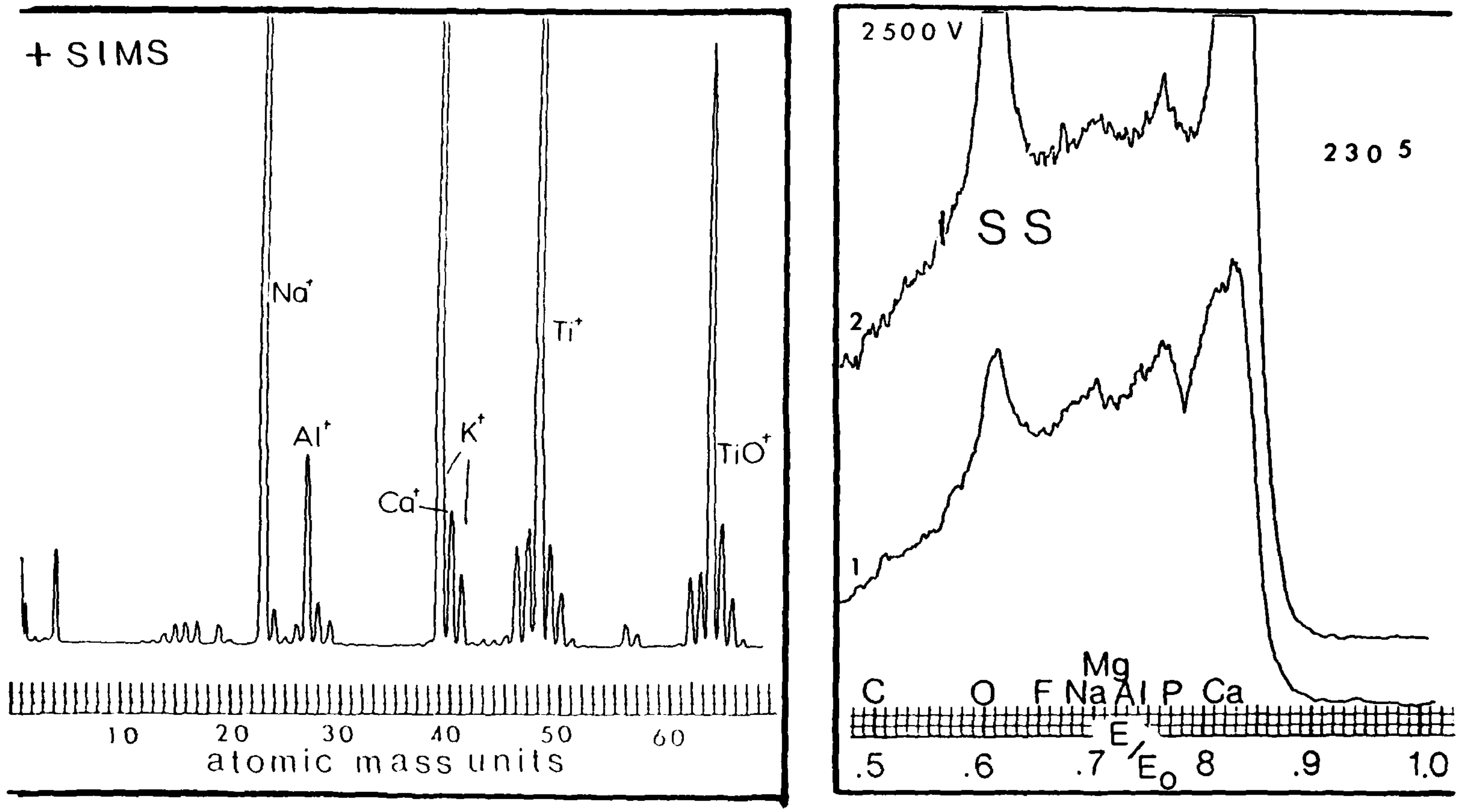


Figure 5. ISS/SIMS Data from Sample 230-5

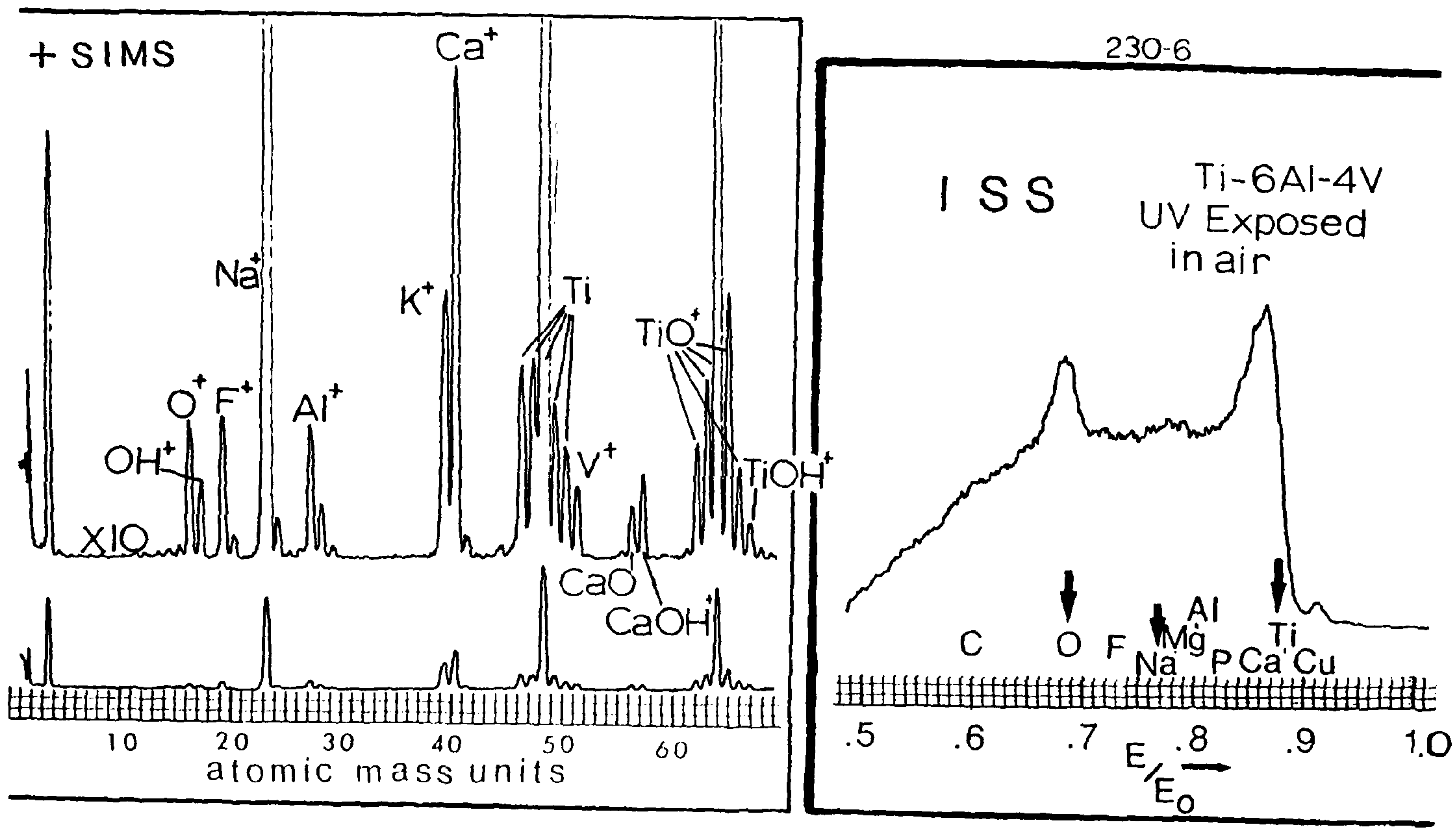


Figure 6. ISS/SIMS Data from Sample 230-6

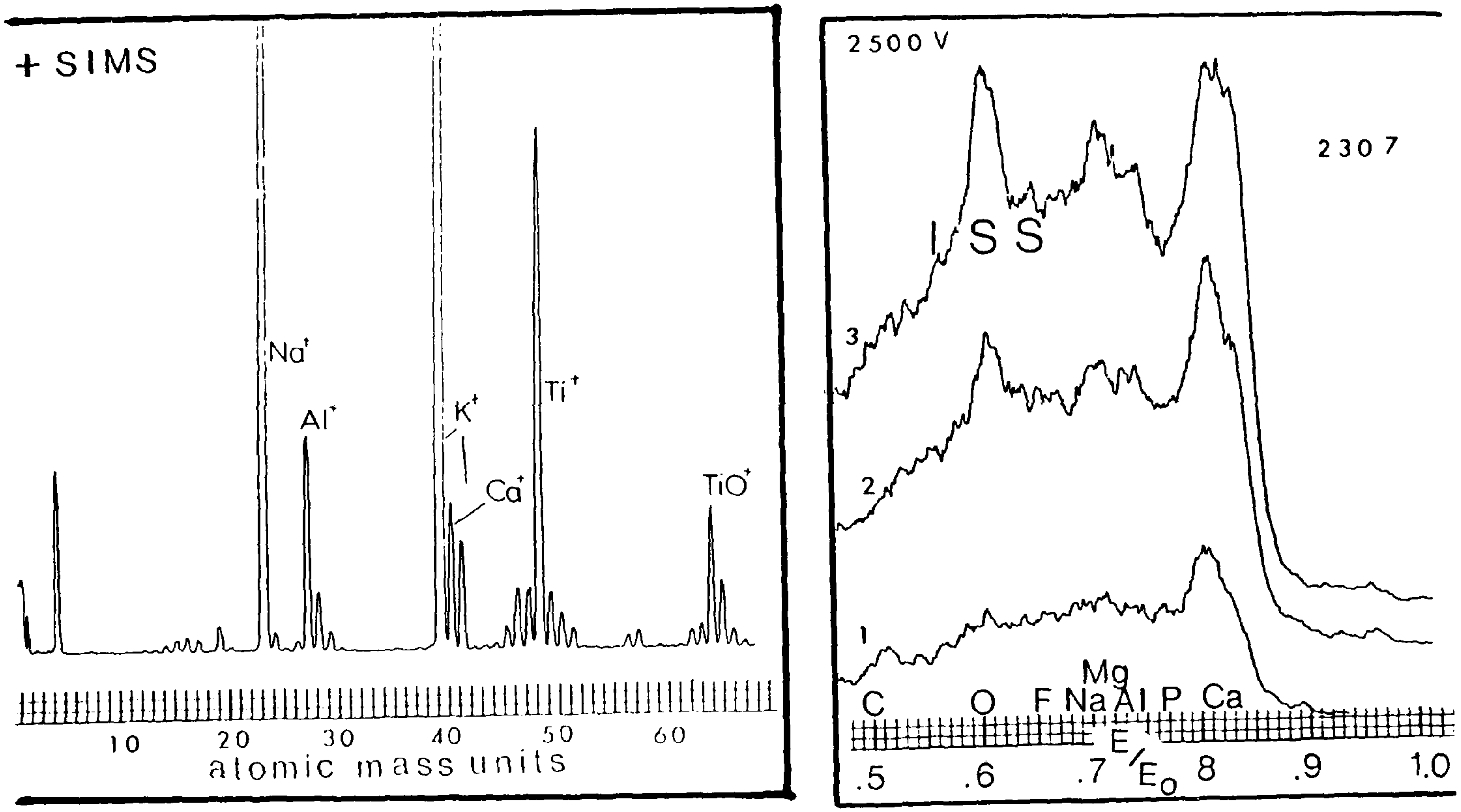


Figure 7. ISS/SIMS Data from Sample 230-7

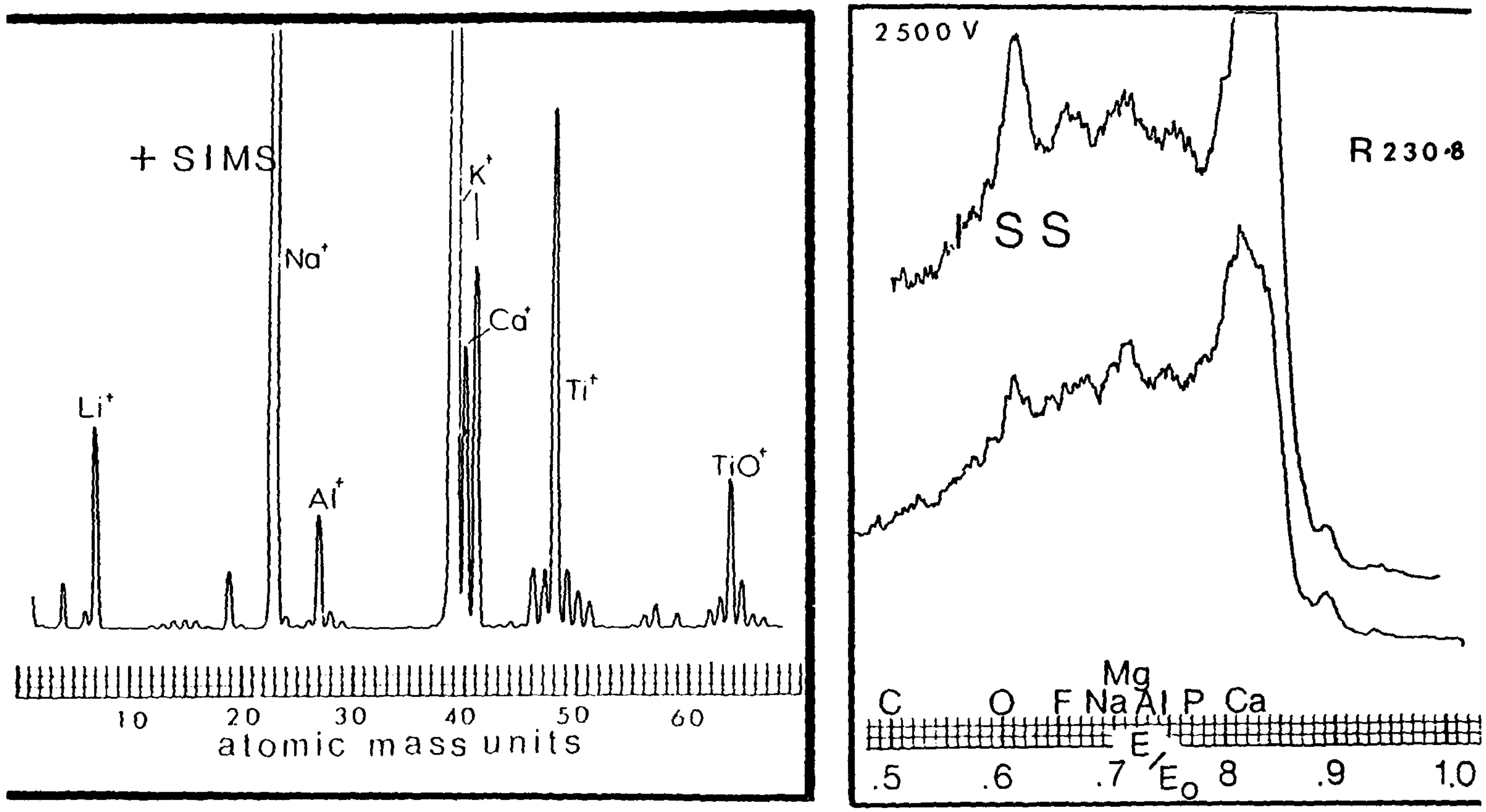


Figure 8. ISS/SIMS Data from Sample 230-8

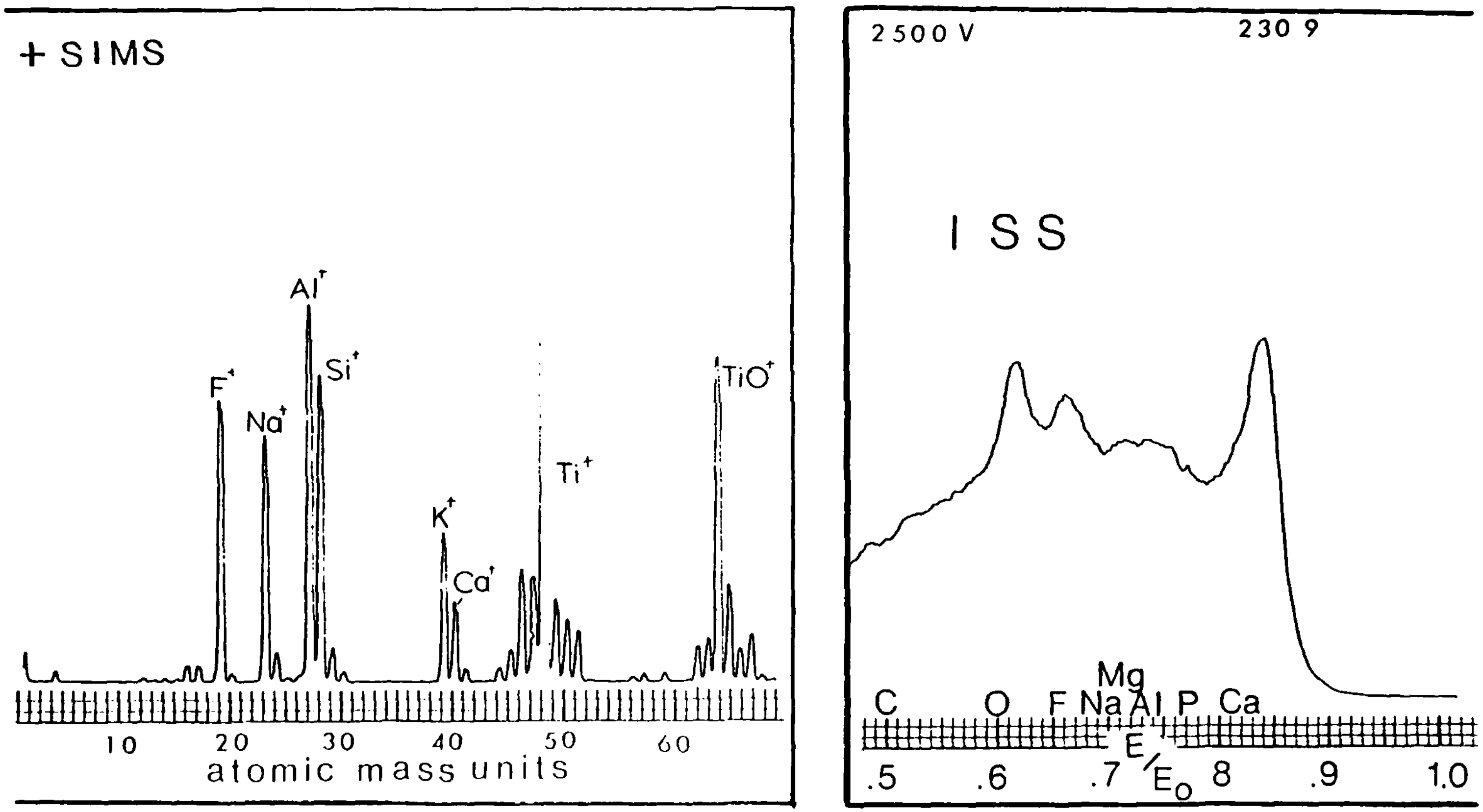


Figure 9. ISS/SIMS Data from Sample 230-9

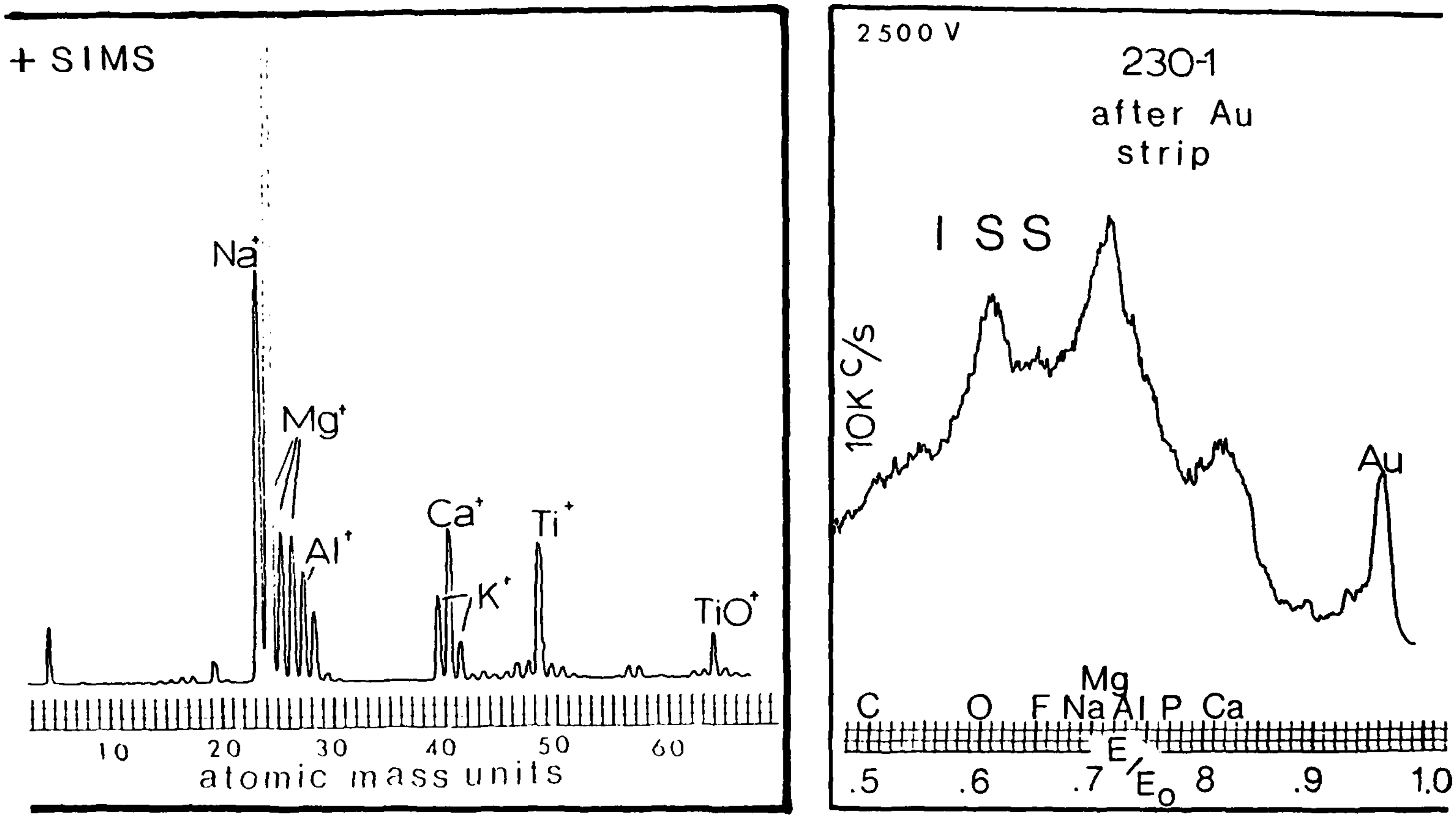


Figure 10. ISS/SIMS Data from Sample 230-1 After Au Strip

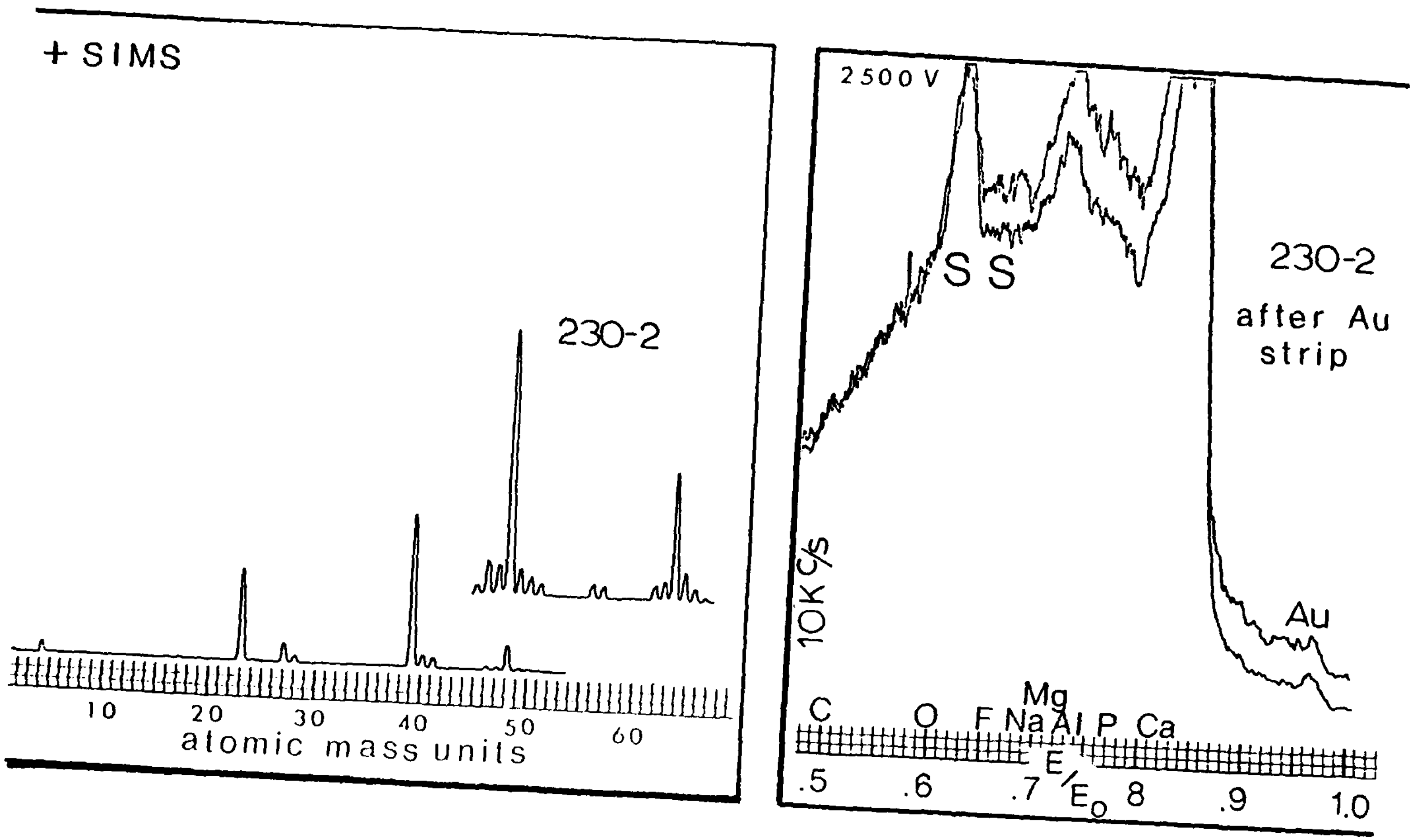


Figure 11. ISS/SIMS Data from Sample 230-2 After Au Strip

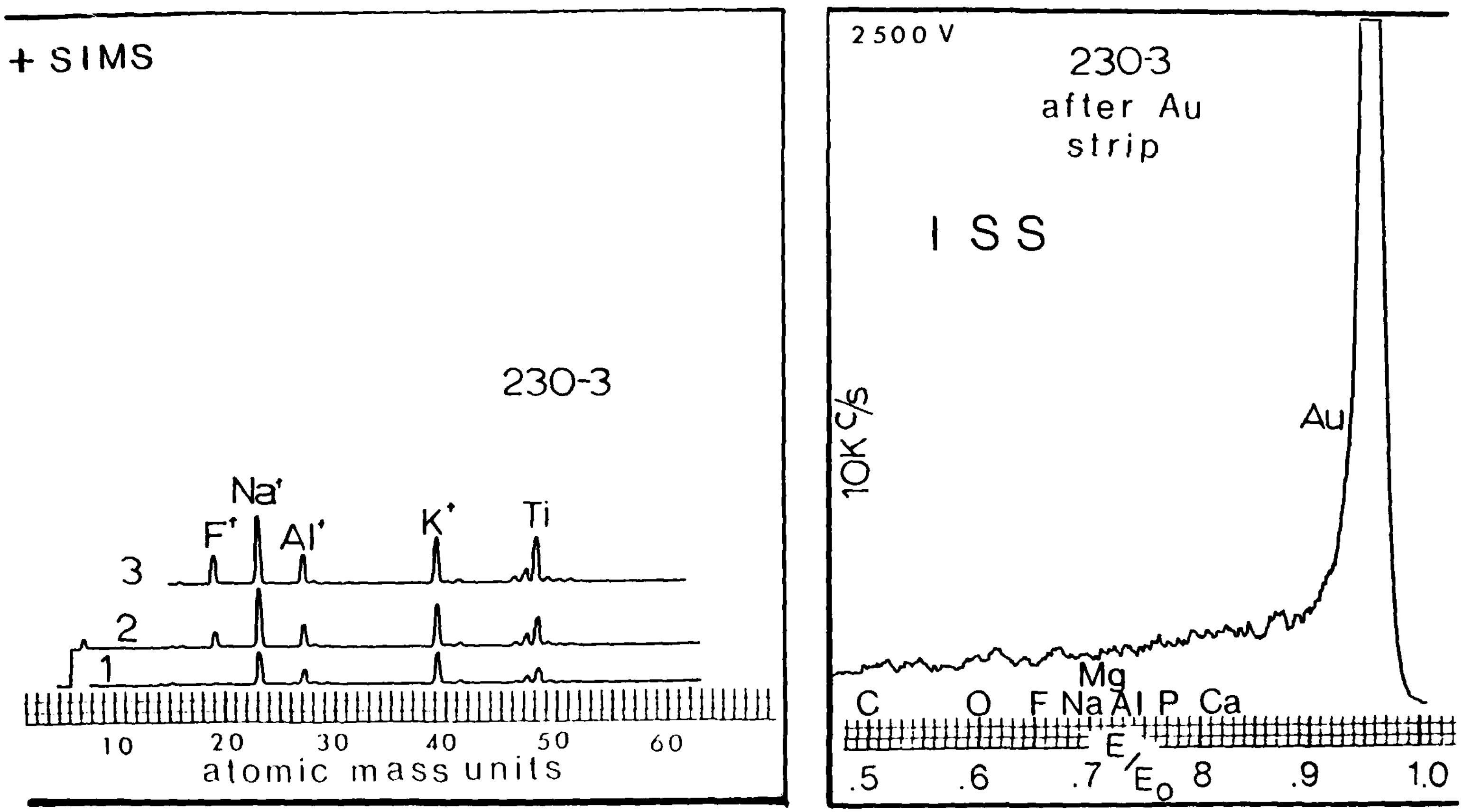


Figure 12. ISS/SIMS Data from Sample 230-3 After Au Strip

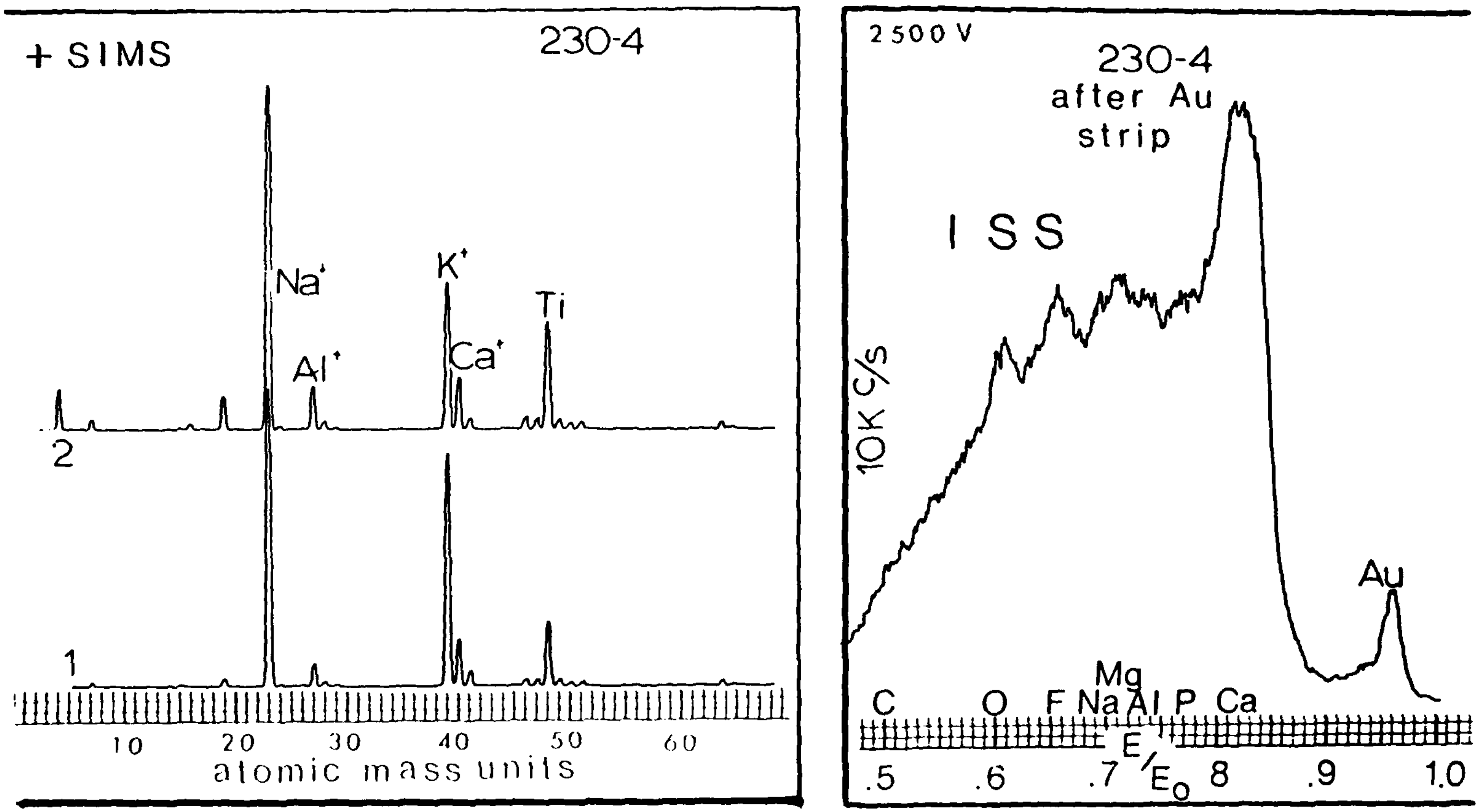


Figure 13. ISS/SIMS Data from Sample 230-4 After Au Strip

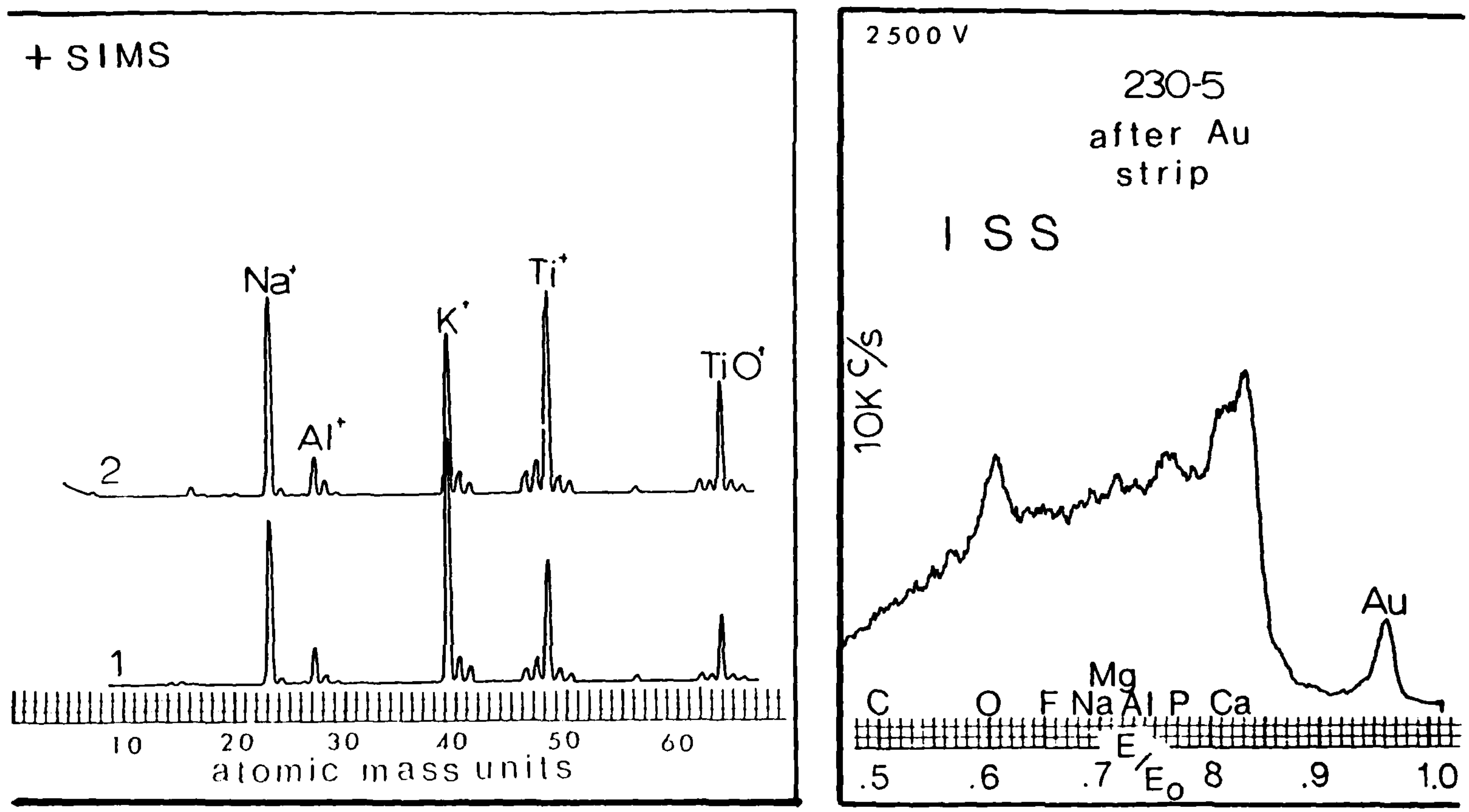


Figure 14. ISS/SIMS Data from Sample 230-5 After Au Strip

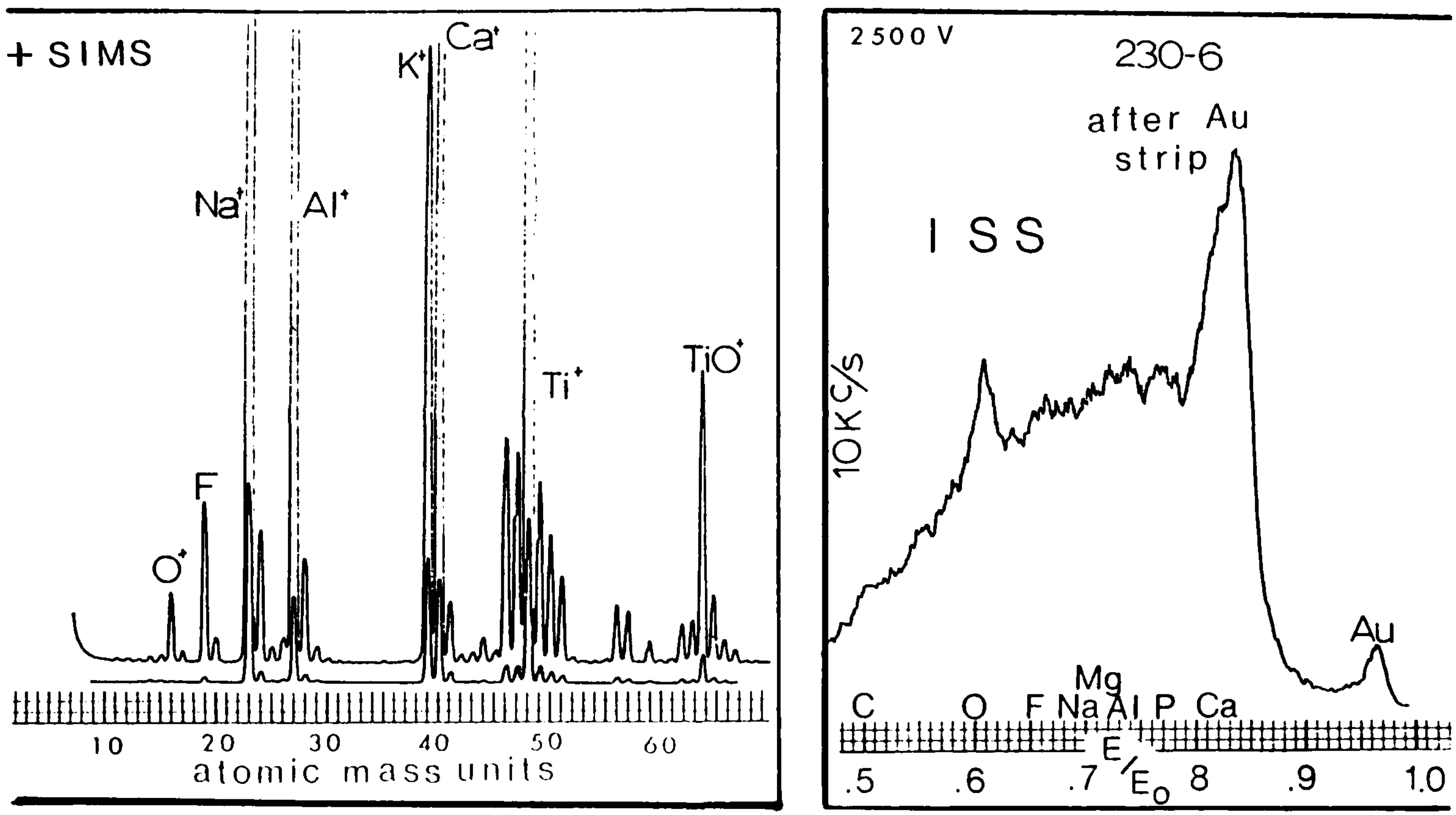


Figure 15. ISS/SIMS Data from Sample 230-6 After Au Strip

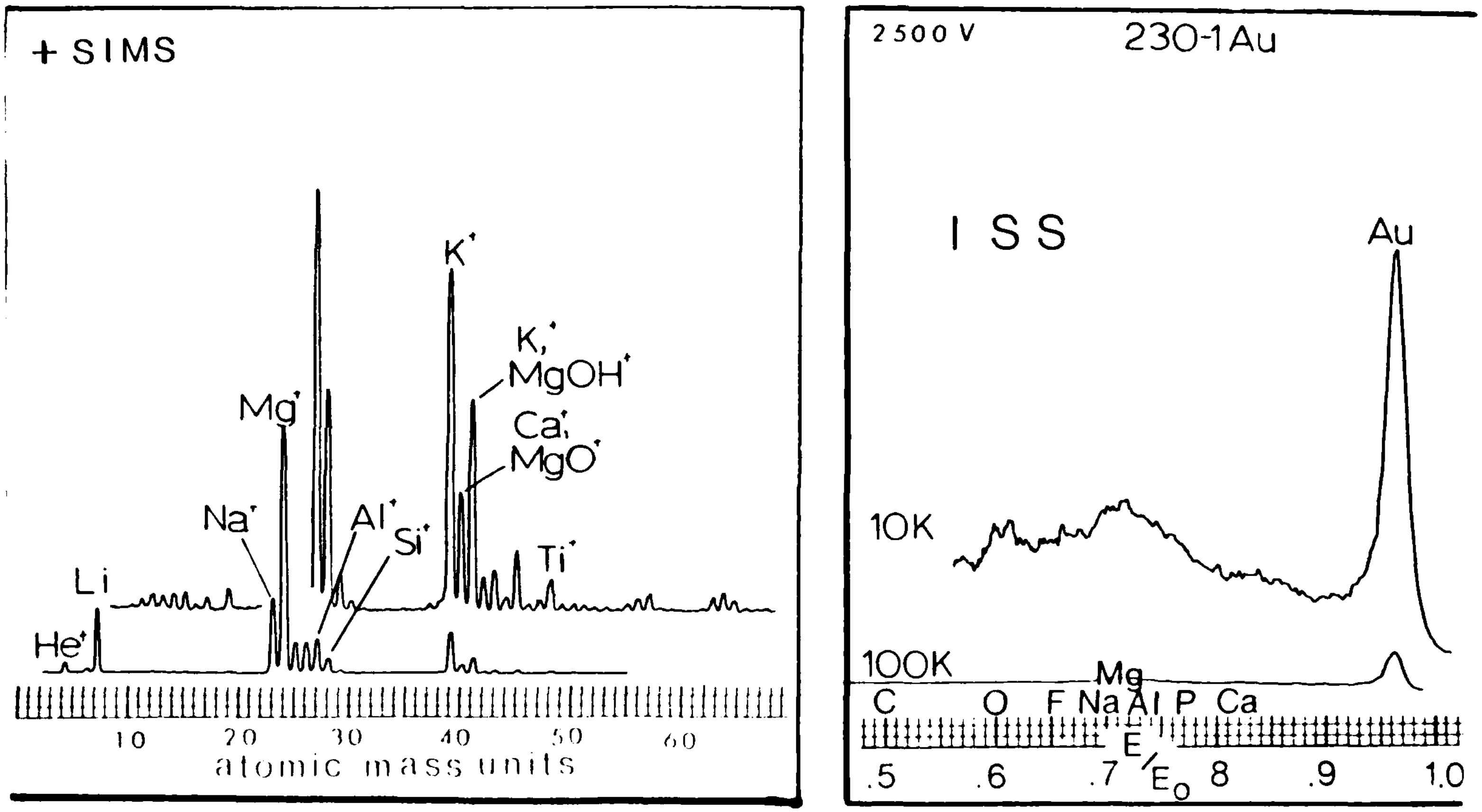


Figure 16. ISS/SIMS Data from Gold Stripped from Sample 230-1

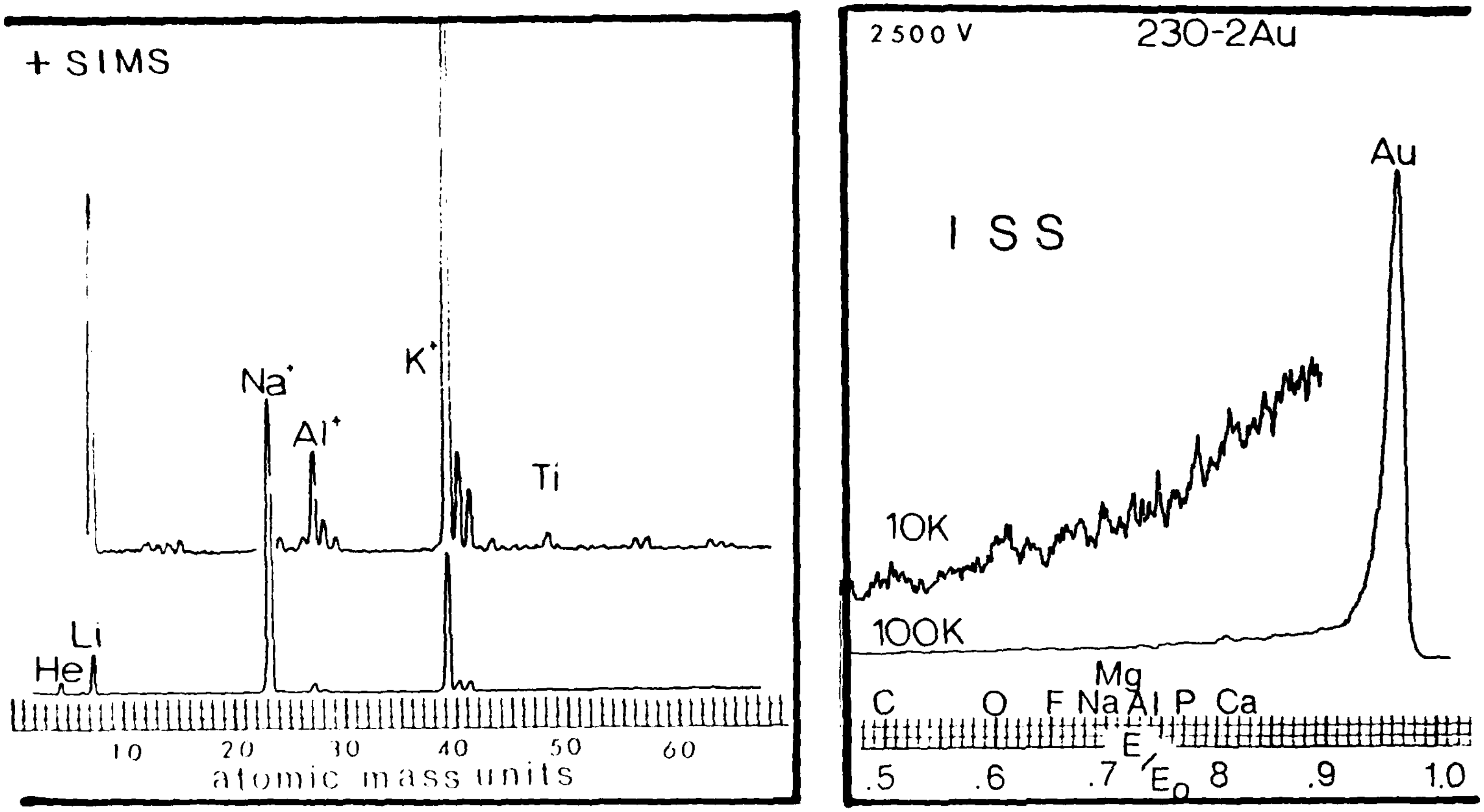


Figure 17. ISS/SIMS Data from Gold Stripped from Sample 230-2

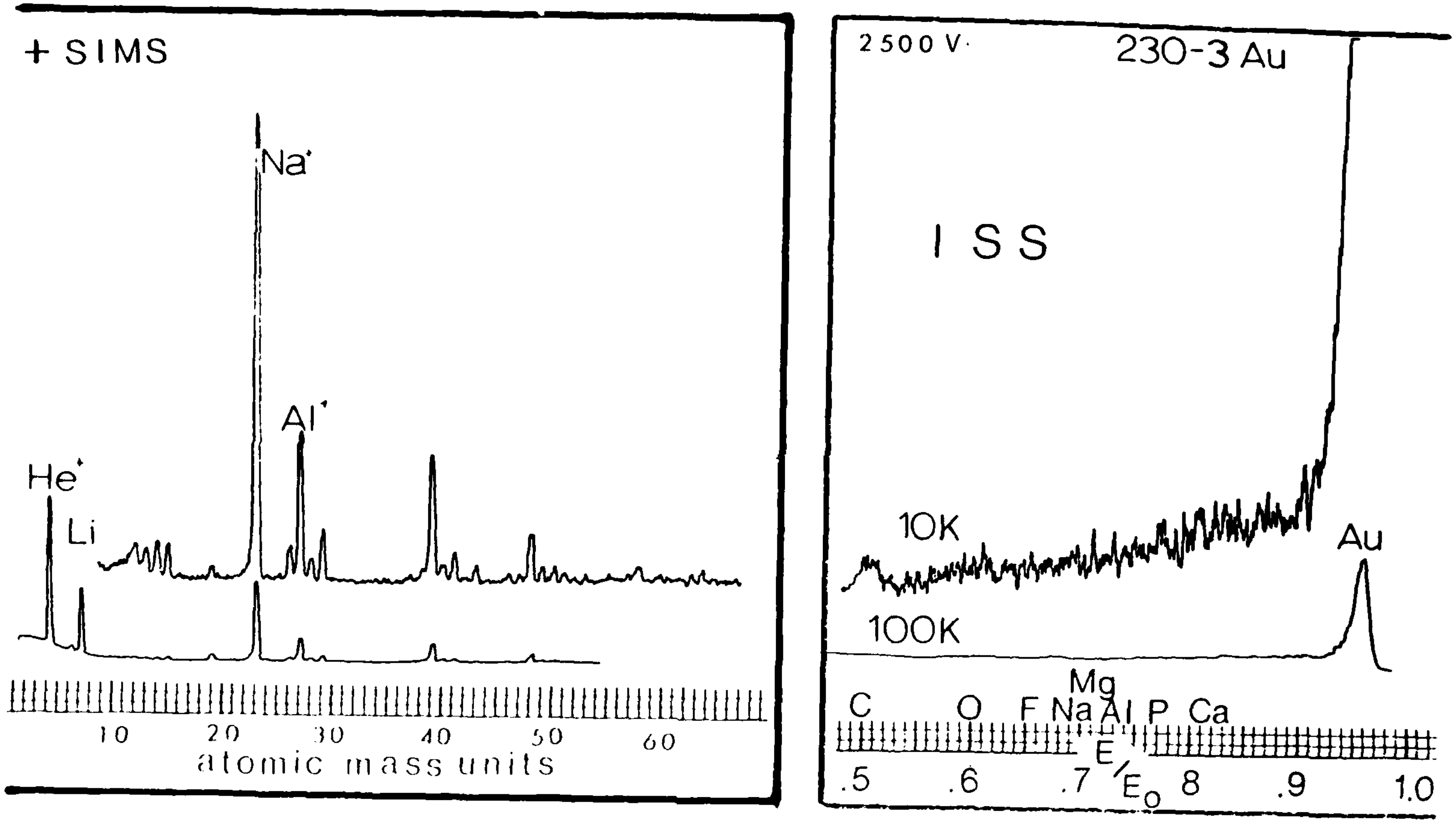


Figure 18. ISS/SIMS Data frum Gold Stripped from Sample 230-3

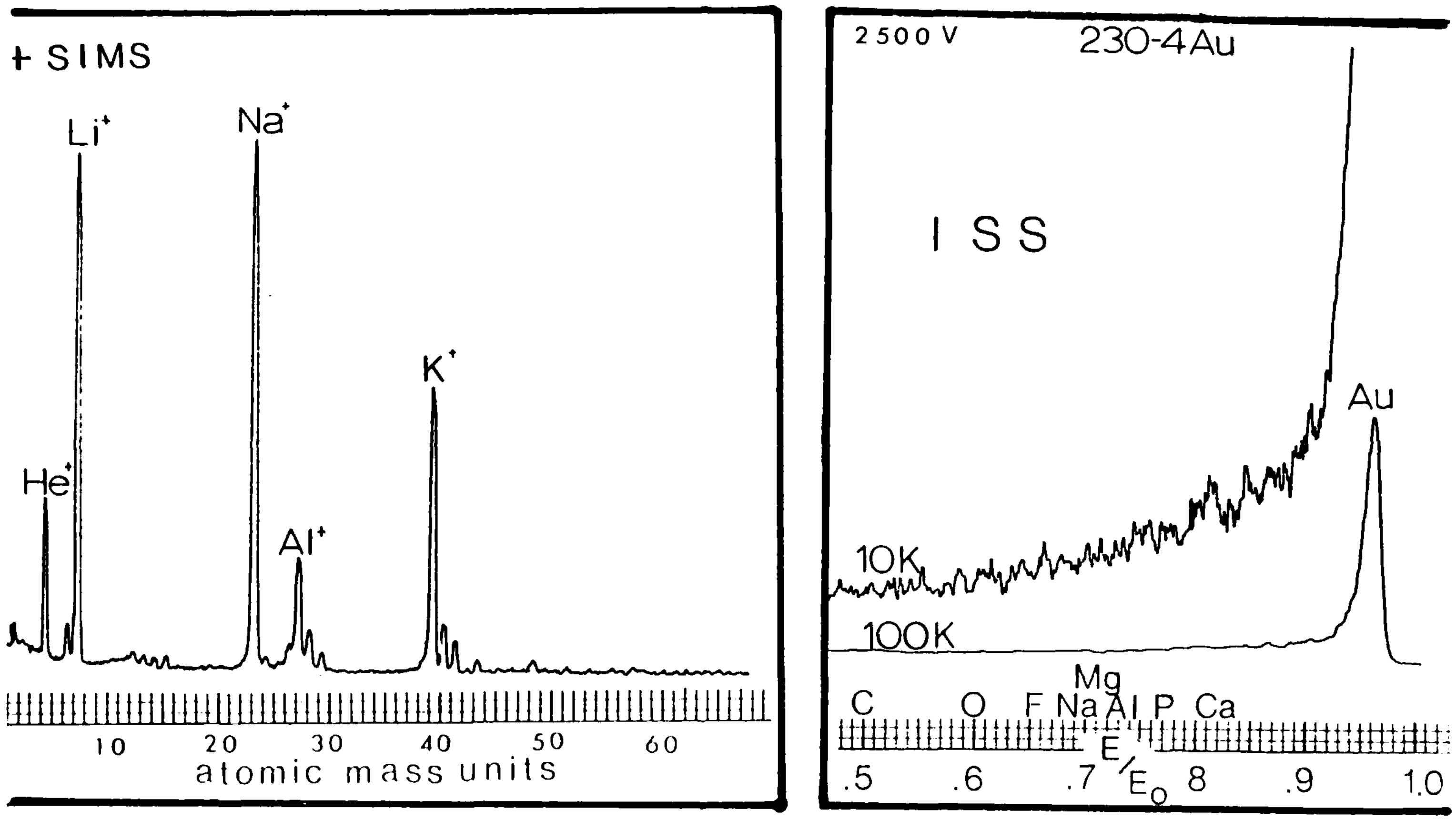


Figure 19. ISS/SIMS Data from Gold Stripped from Sample 230-4

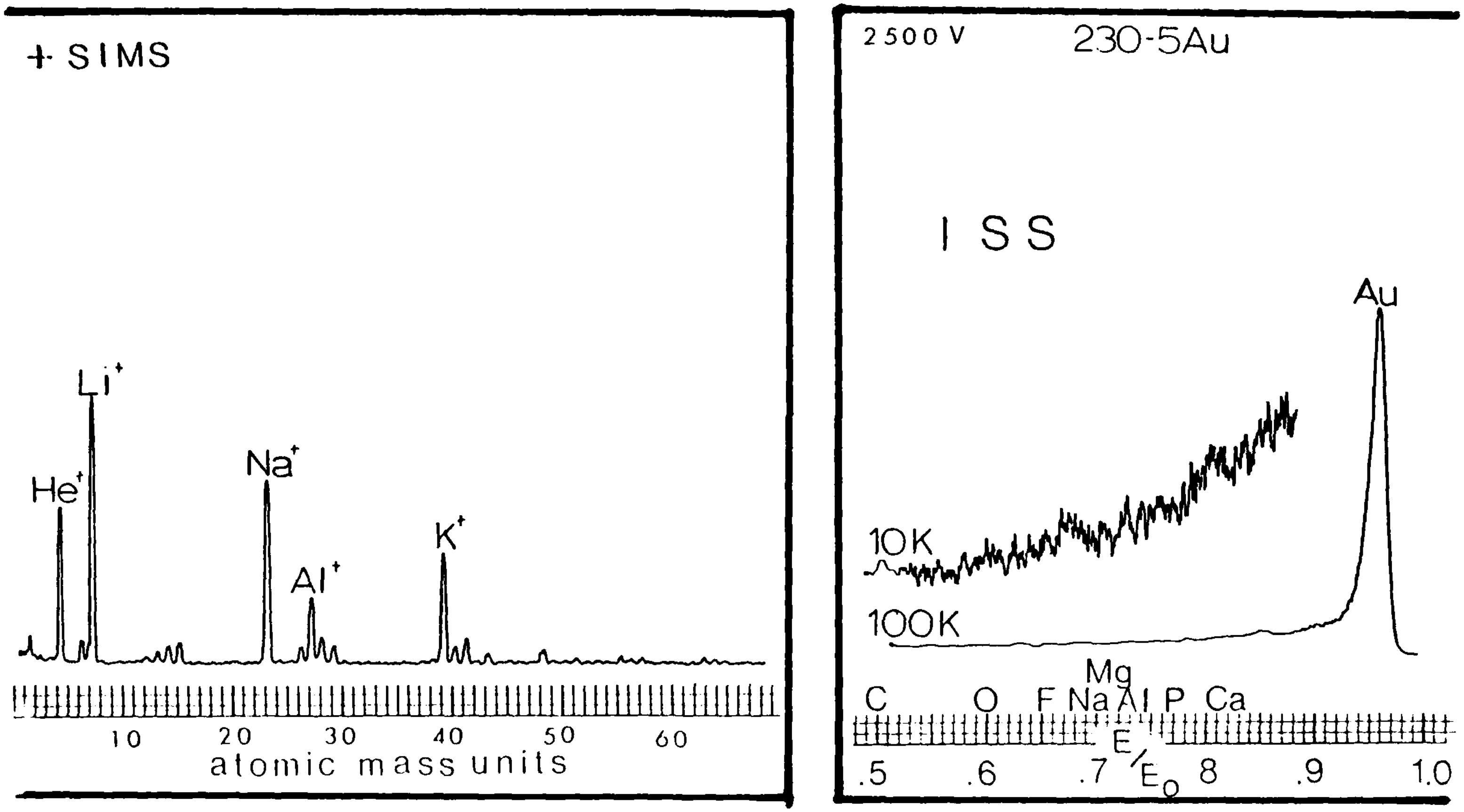


Figure 20. ISS/SIMS Data from Gold Stripped from Sample 230-5

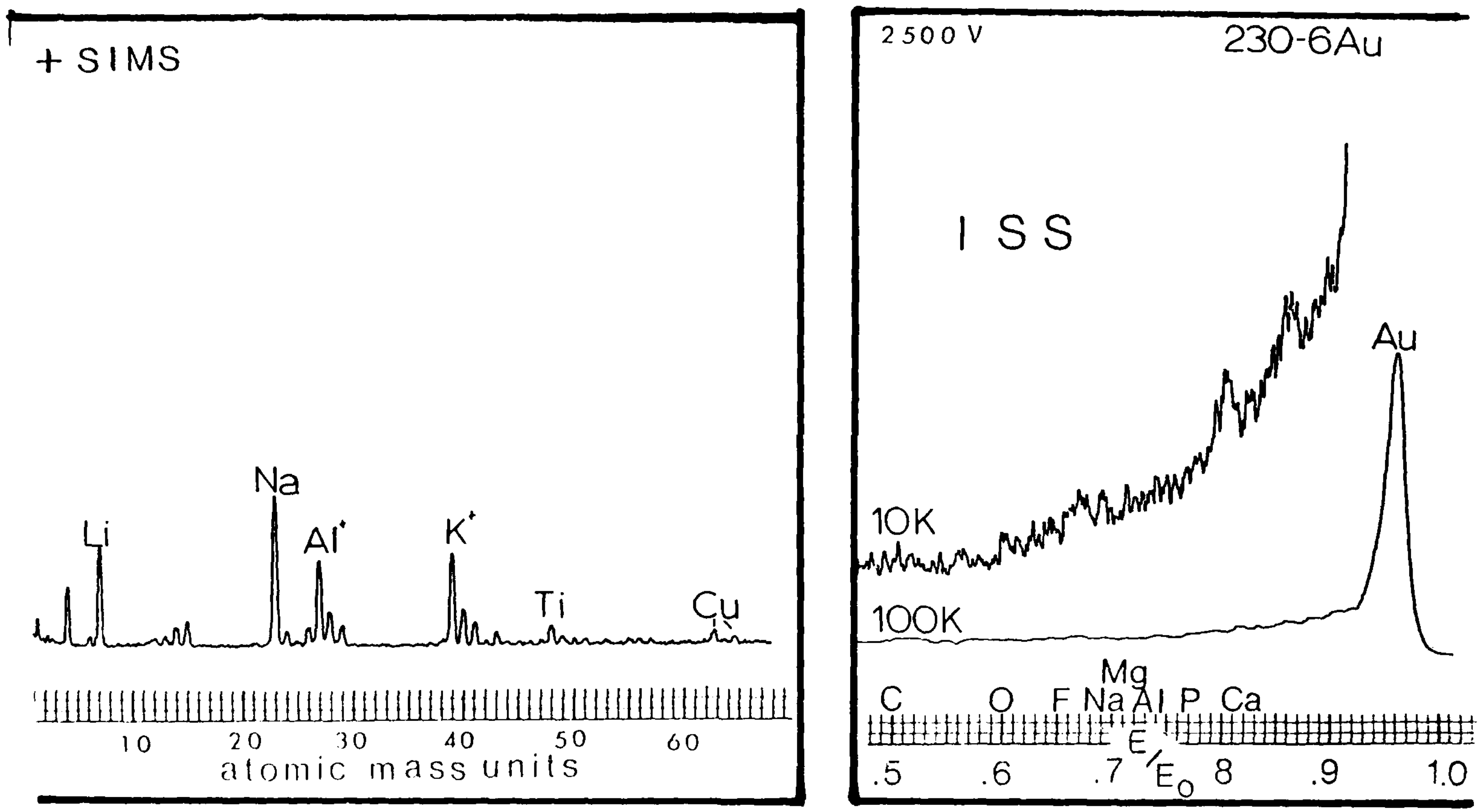


Figure 21. ISS/SIMS Data from Gold Stripped from Sample 230-6

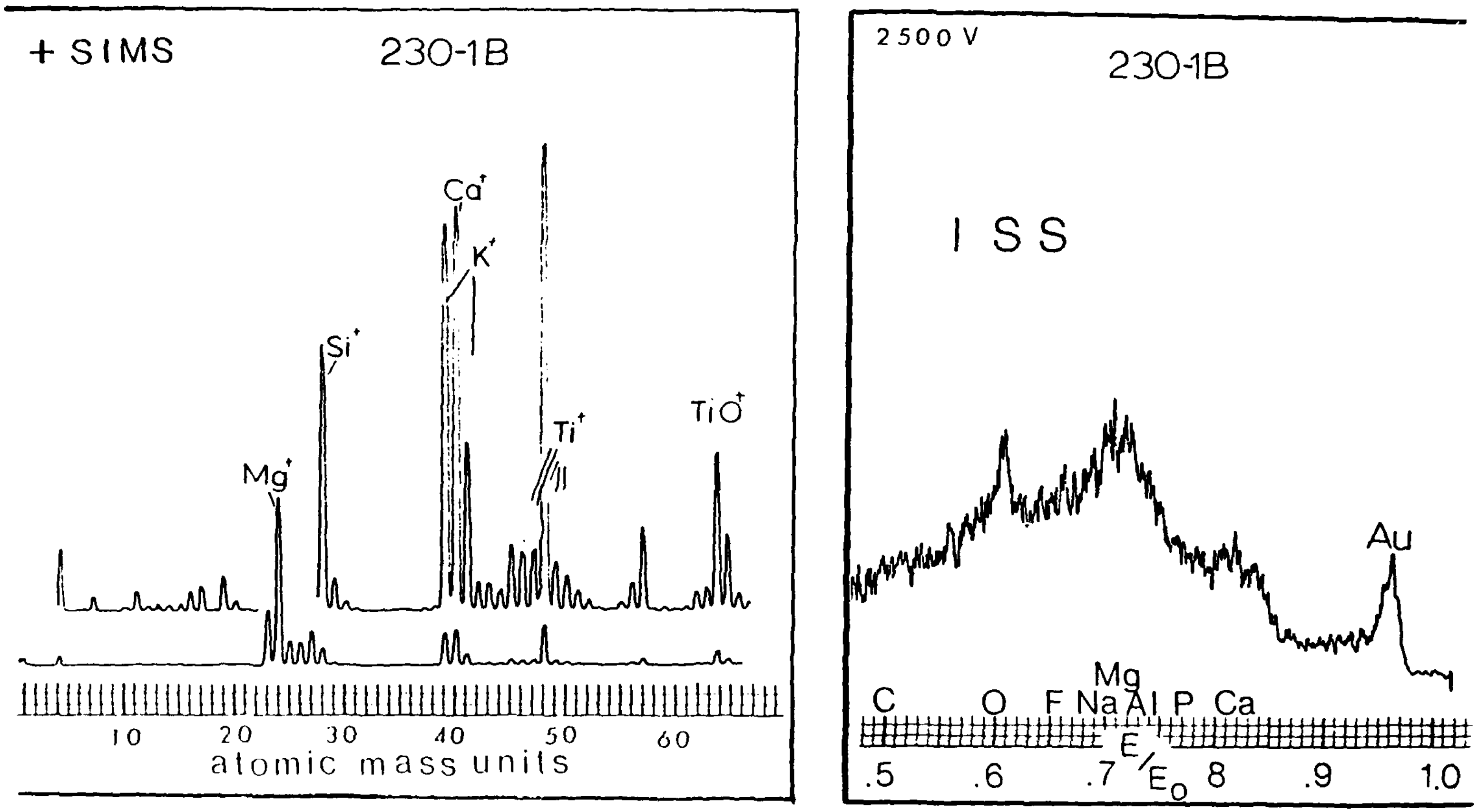


Figure 22. ISS/SIMS Data from Sample 230-1 Following Humid Age and Gold Strip

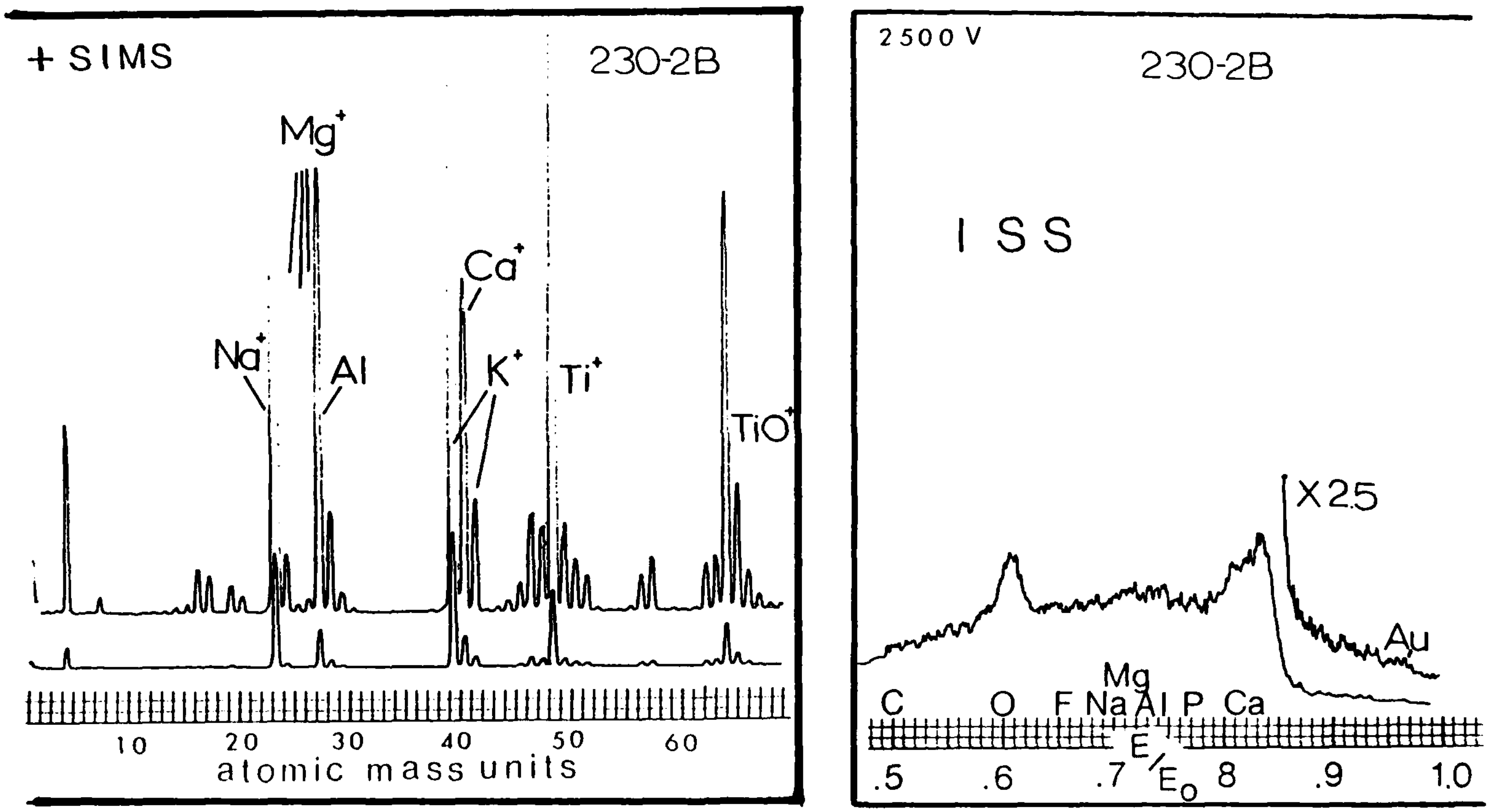


Figure 23. ISS/SIMS Data from Sample 230-2 Following Humid Age and Gold Strip

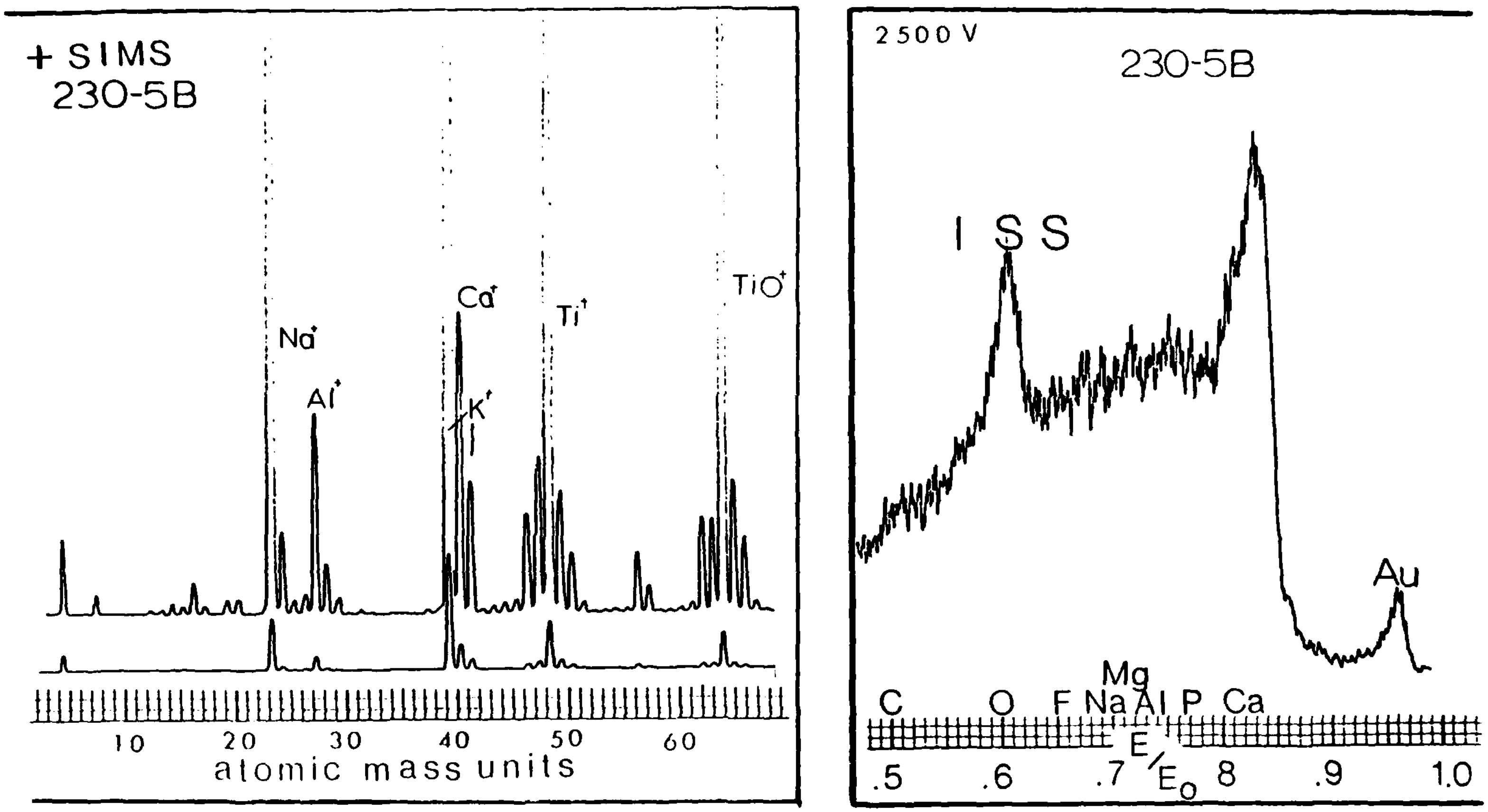


Figure 24. ISS/SIMS Data from Sample 230-5 Following Humid Age and Gold Strip

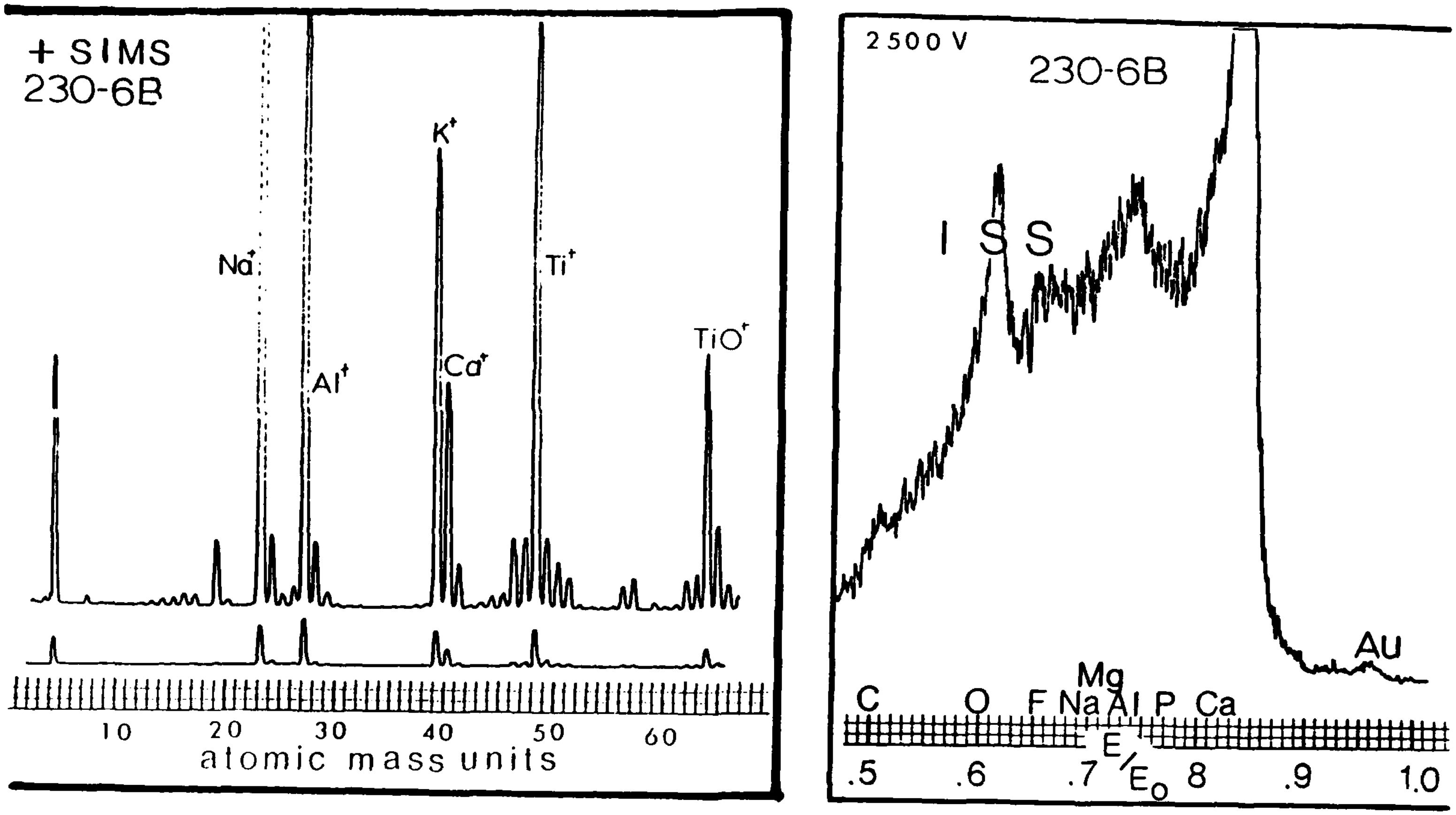


Figure 25. ISS/SIMS Data from Sample 230-6 Following Humid Age and Gold Strip

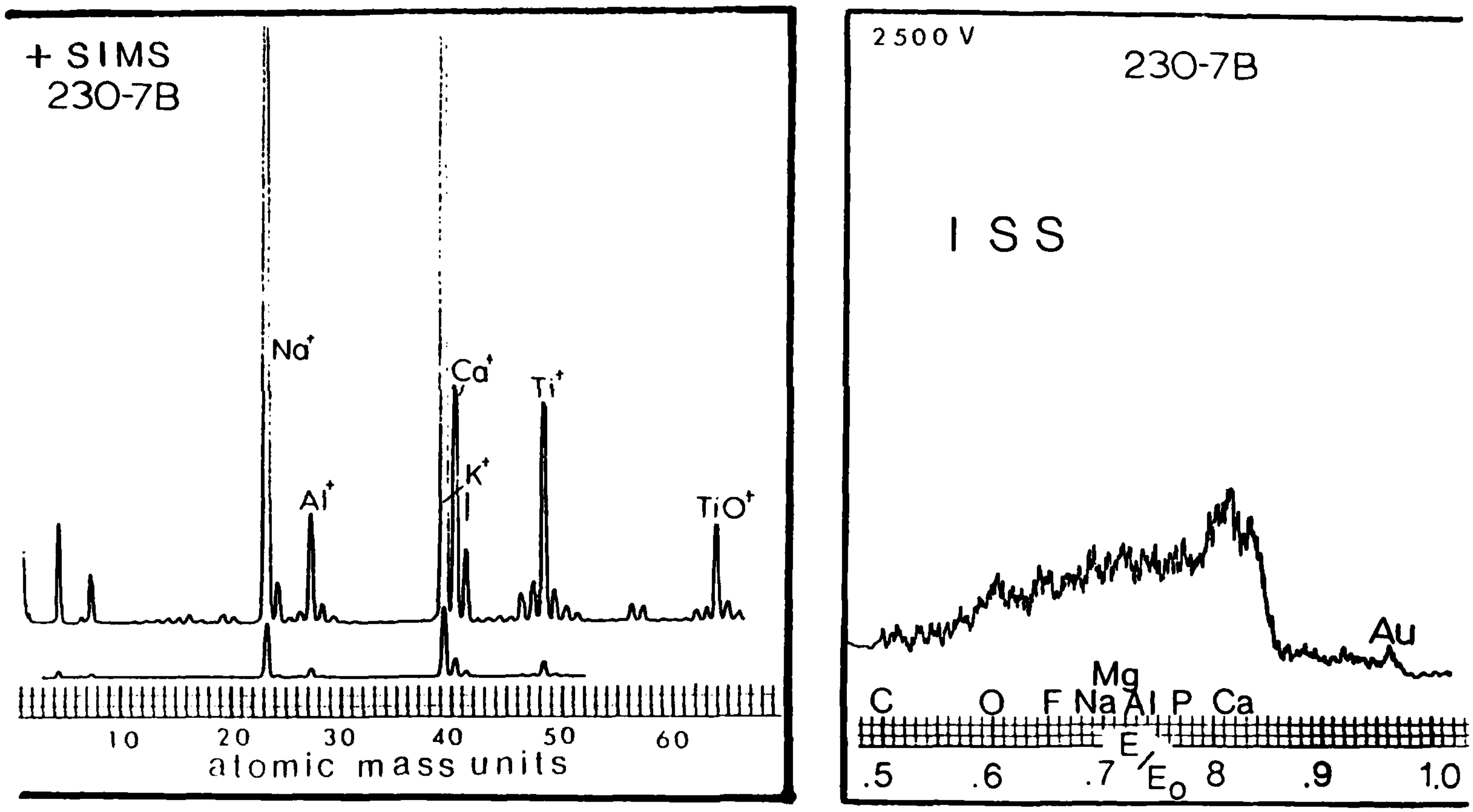


Figure 26. ISS/SIMS Data from Sample 230-7 Following Humid Age and Gold Strip

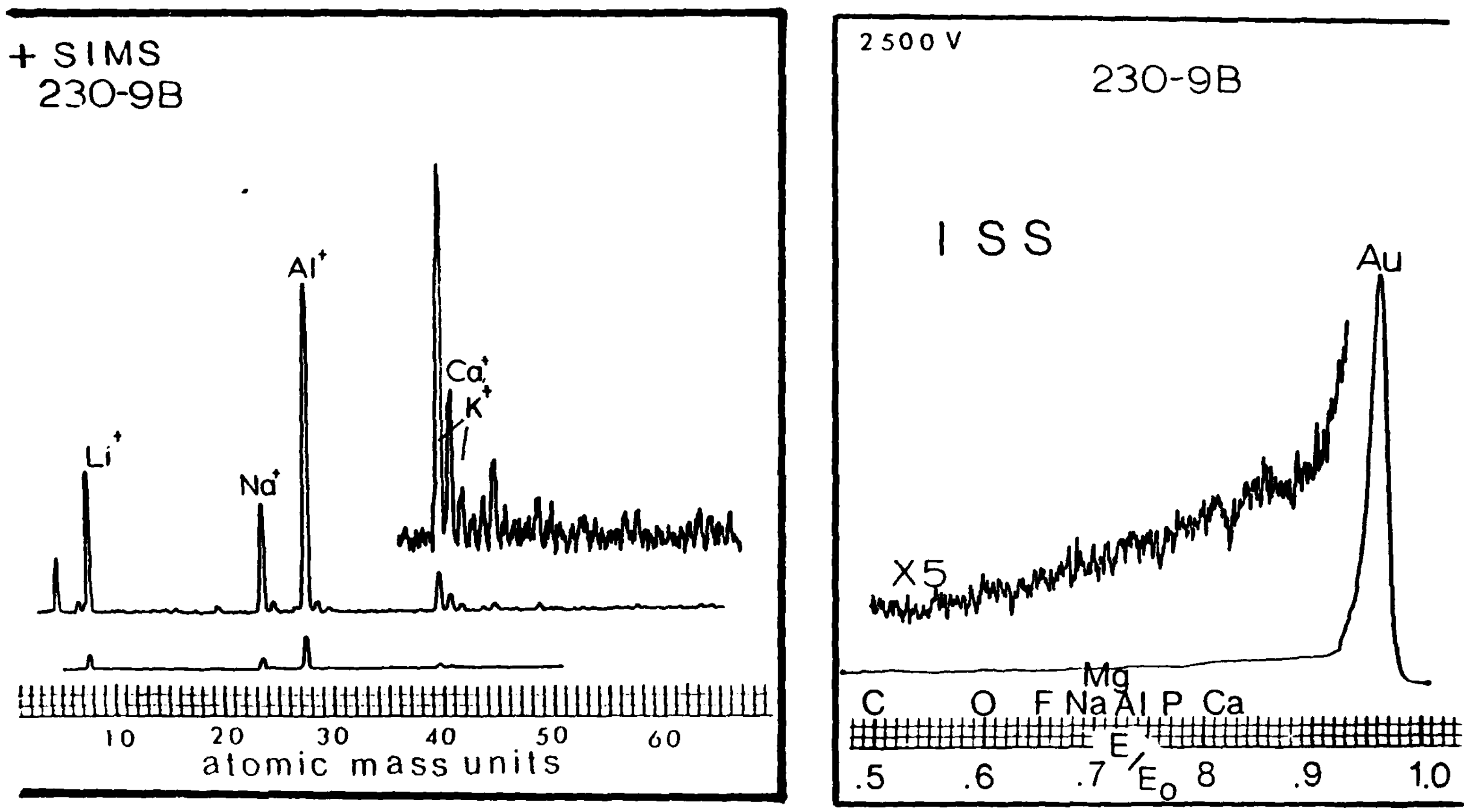


Figure 27. ISS/SIMS Data from Sample 230-9 Following Humid Age and Gold Strip

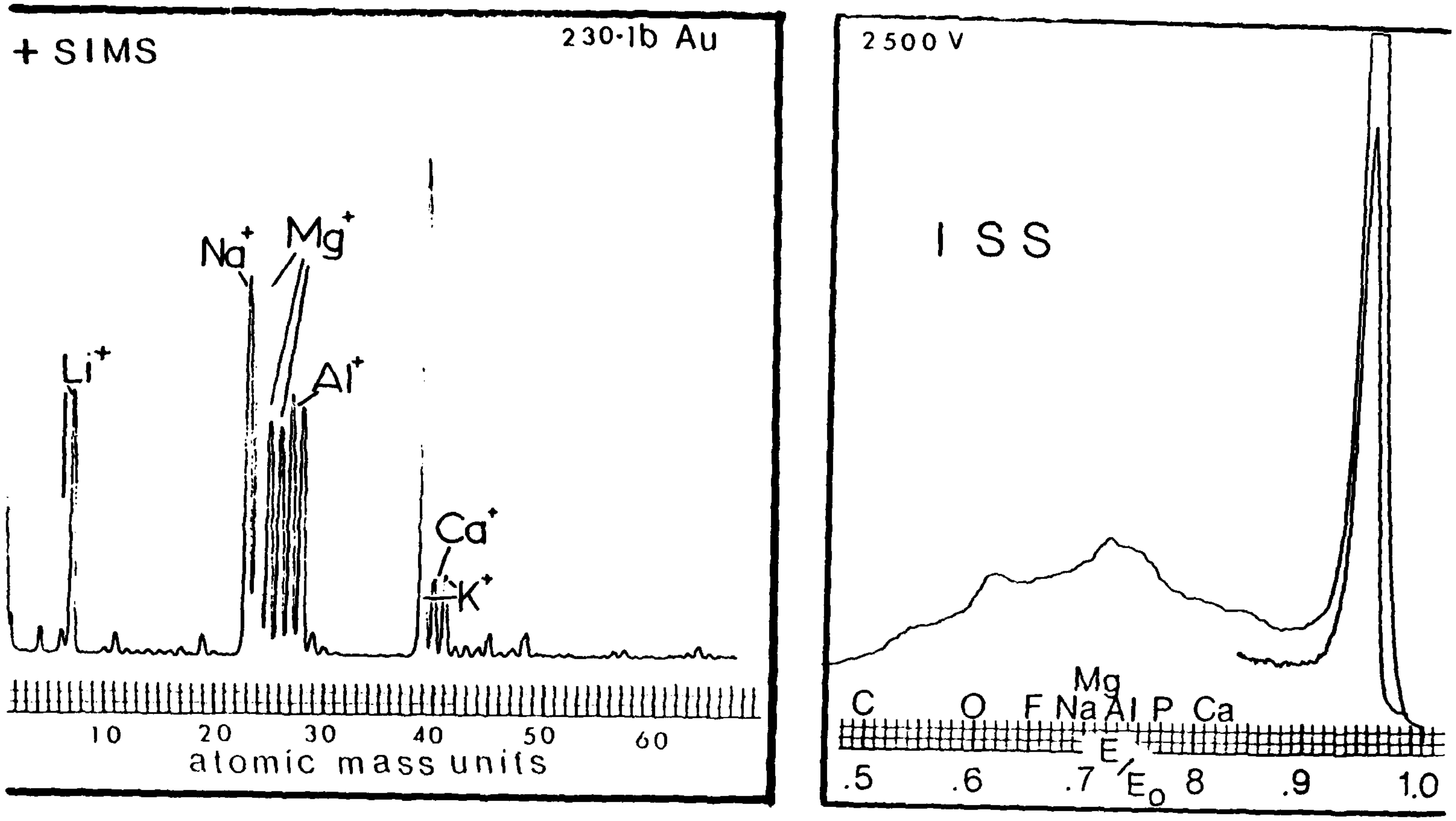


Figure 28. *ISS/SIMS Data from Gold Stripped from Sample 230-1 Following Humid Age*

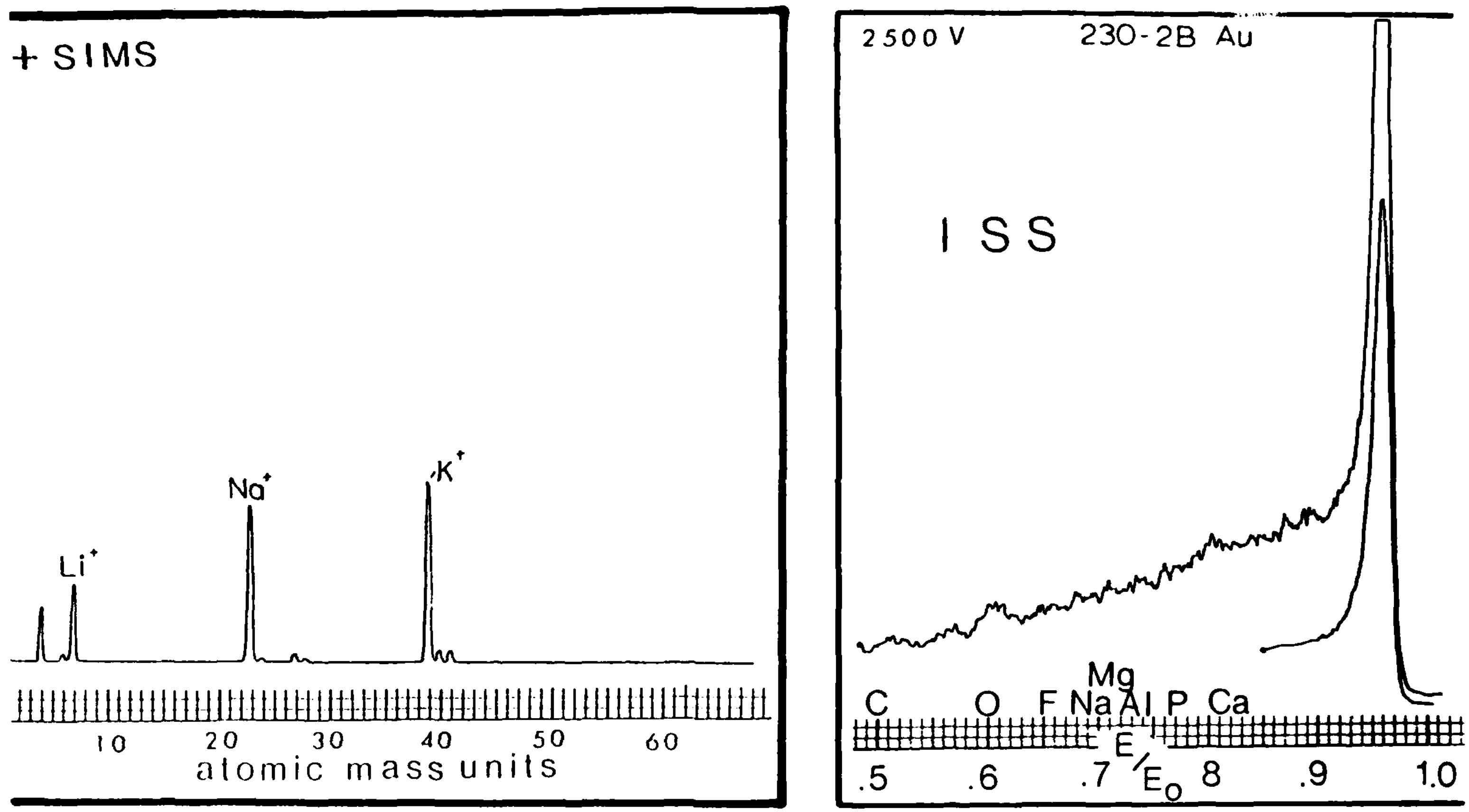


Figure 29. ISS/SIMS Data from Gold Stripped from Sample 230-2 Following Humid Age

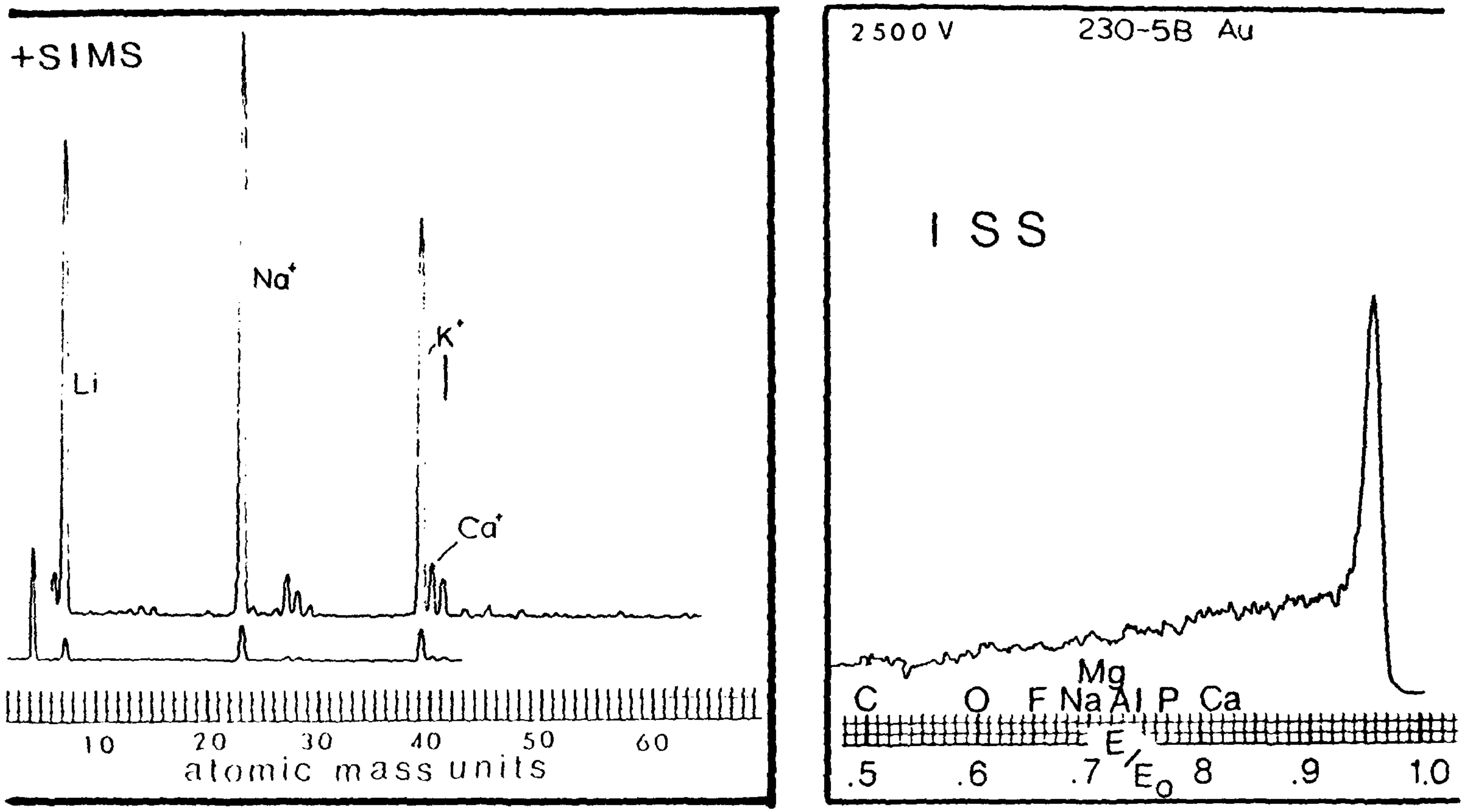


Figure 30. ISS/SIMS Data from Gold Stripped from Sample 230-5 After Humid Age

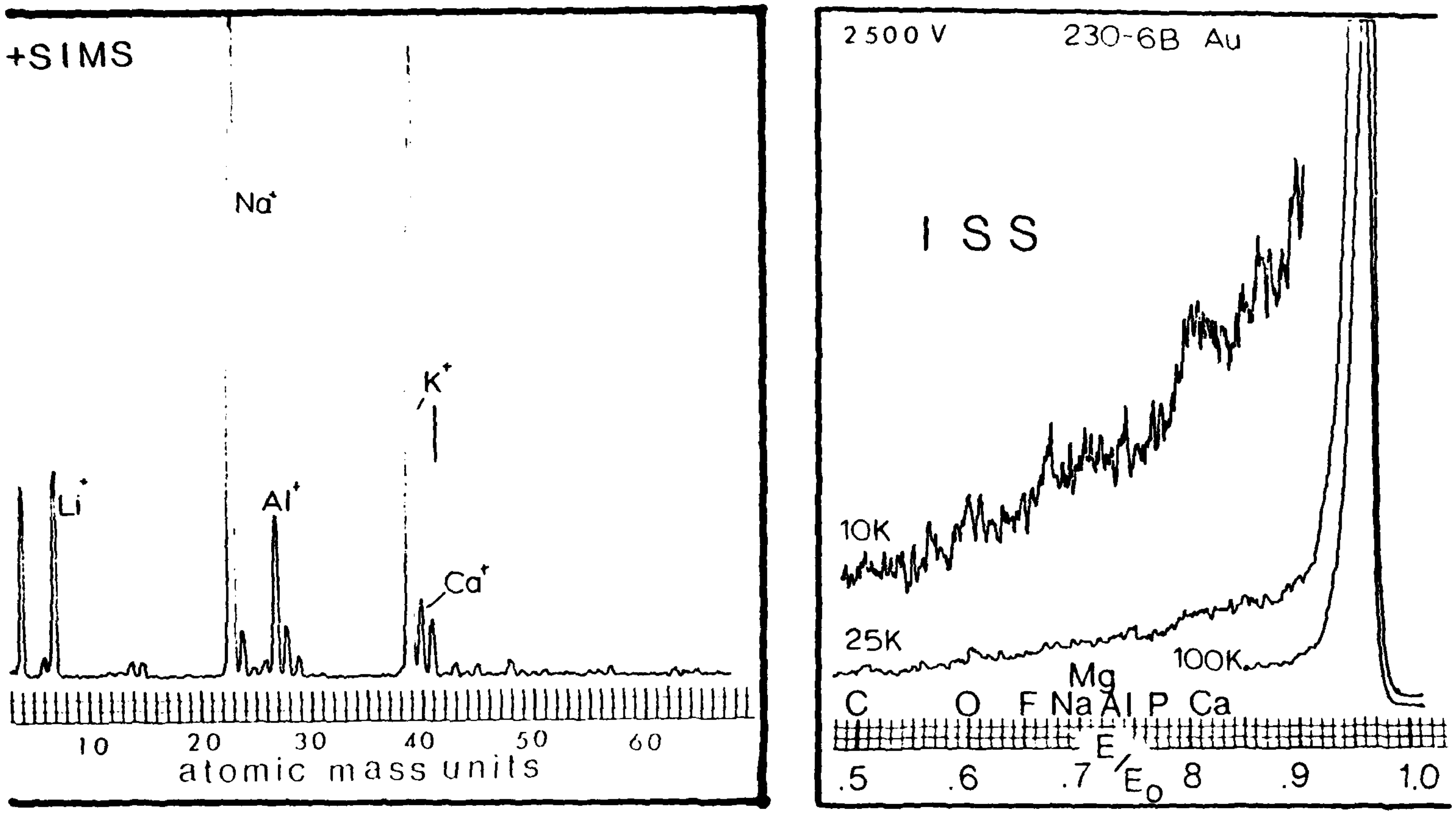


Figure 31. ISS/SIMS Data from Gold Stripped from Sample 230-6 Following Humid Age

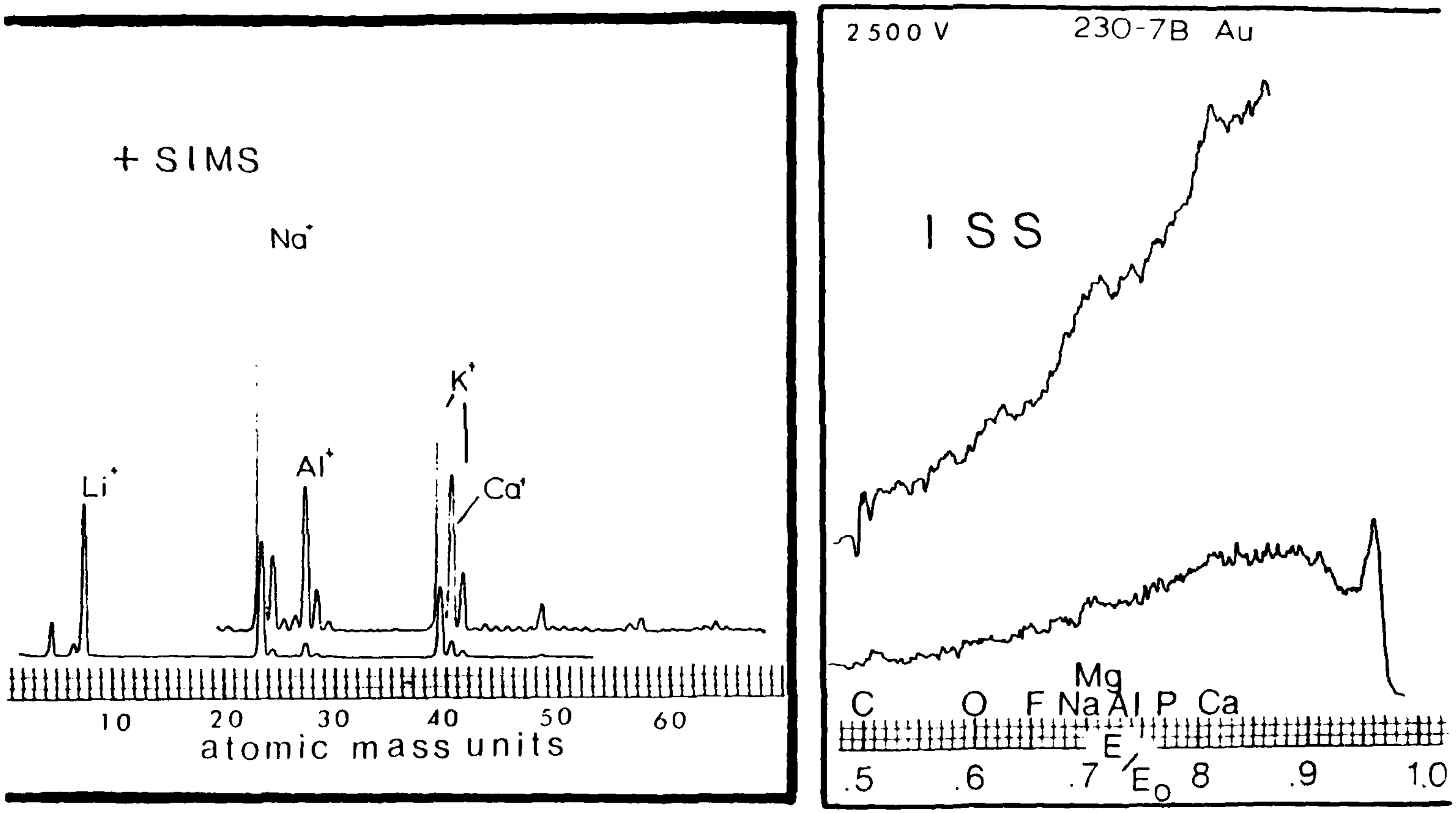


Figure 32. ISS/SIMS Data from Gold Stripped from Sample 230-7 Following Humid Age

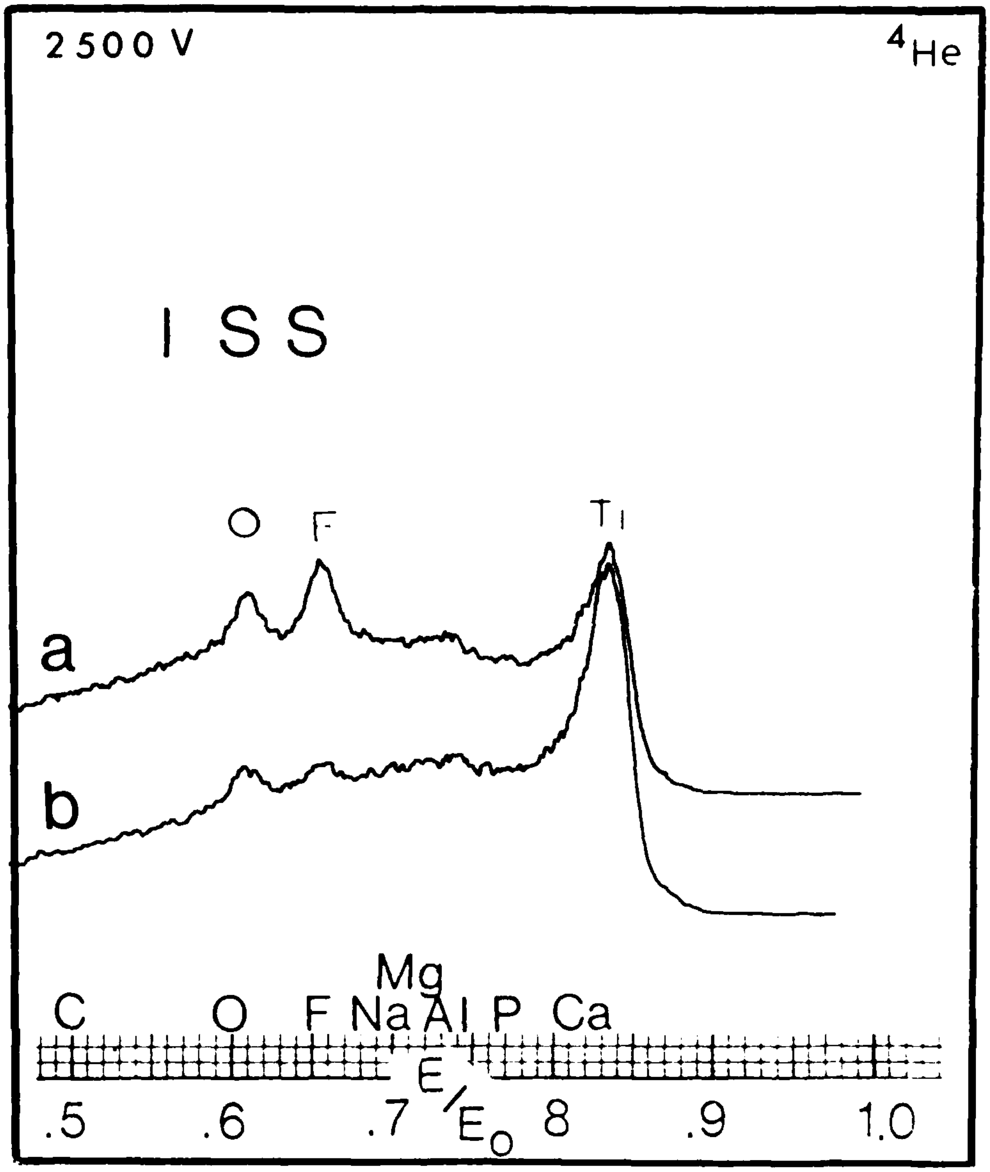


Figure 33. Ion Scattering Spectra from Oxide-Alloy Failure Surface a. Oxide Surface b. Alloy Surface

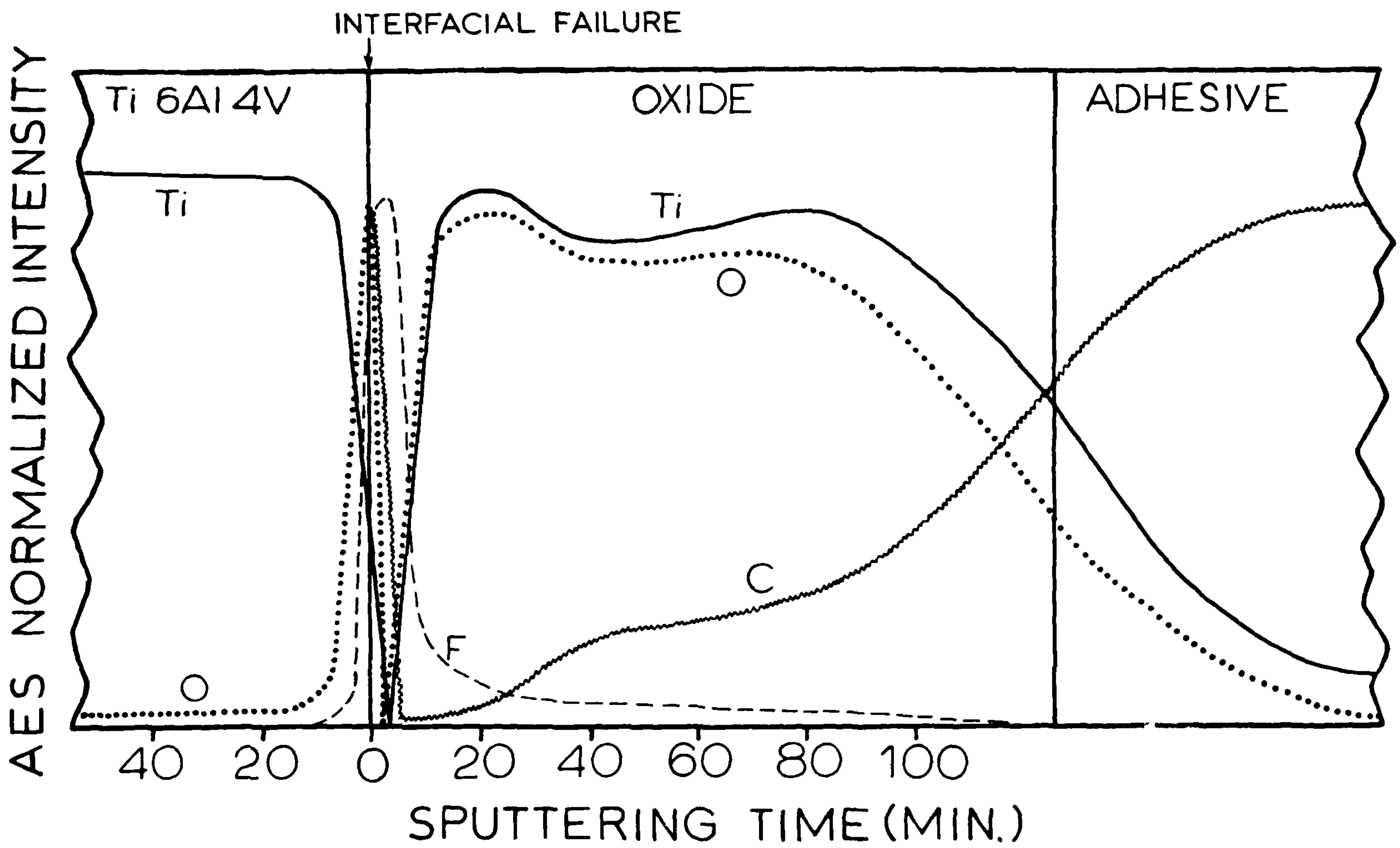


Figure 34. Elemental Profile through Interfaces in Anodized Oxide on Ti6Al4V Obtained by AES

☆U.S.Government Printing Office: 1980 — 657-084/487